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Radical Reduction of Cyclic Xanthates: Formation of Alkenes and/or 1,3-Oxathiolanes from 1,3-Oxathiolane-2-thiones

Jun'ichi Uenishi,* Takayuki Kunugi, and Yuki Kubo

Department of Chemistry, Okayama University of Science, Ridaicho, Okayama 700, Japan

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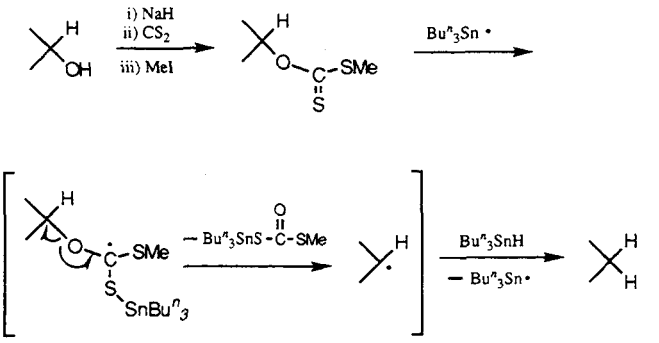
ABSTRACT

AIBN-initiated radical reactions of 5-membered cyclic xanthates, 1,3-oxathiolane-2-thiones, with tributyltin hydride are described. Alkenes are formed at 0.025 M concentration of tributyltin hydride, whereas a higher concentration (0.25 M) gives 1,3-oxathiolanes. A mixture of alkene and 1,3-oxathiolane is obtained by use of intermediate concentrations. Reactions of cis- and trans-4,5-dialkyl-1,3-oxathiolane-2-thiones with tributyltin hydride afford E-alkenes stereoselectively. For an application of this alkene formation reaction, geraniol has been converted to linalool silyl ether in good yield.

INTRODUCTION

Tin hydride has been used extensively as an important reagent in organic synthesis [1]. Since Barton first reported the radical reduction of a xanthate ester with tributyltin hydride, initiated by AIBN [2], various types of thiono derivatives have been subjected to the reduction [3]. Among them, formation of a xanthate ester of a secondary alcohol and successive tin hydride reduction is now a common protocol for deoxygenation of such an alcohol [2]. This reaction has been reviewed by Barton et al. [4], and the reaction mechanism is recognized to be the following [4,5]. An initial addition of a tin radical to a thione group forms a stannylthiocarbo radical intermediate. Then, homolysis of the C–O bond at the β position liberates a dithiocarbonate and a secondary alkanyl radical, which is subsequently reduced by another tin hydride molecule to give an alkane. In the last step, a tin radical is regenerated and starts a new reduction cycle. In other words, a multistep radical chain reaction is operative.



SCHEME 1

However, the only reduction of a cyclic xanthate with tributyltin hydride that has been reported by Williams and Moore [6], in which some 1,3-oxathiolane-2-thione derivatives, on treatment with tributyltin hydride, gave 1,3-oxathiolanes, as shown in Scheme 2.

We have now examined the radical reduction of 5-membered cyclic xanthates, 1,3-oxathiolane-2-thiones, and found that tributyltin hydride/AIBN treatment gives not only 1,3-oxathiolane but also the corresponding alkene, as shown in Scheme 3. The ratios of the products were found to depend on the concentration of tributyltin hydride. In this article, the details of these reactions are described.

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

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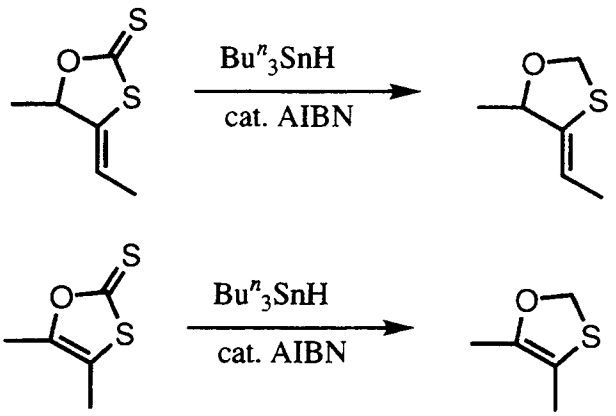
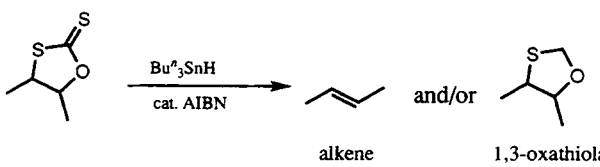


SCHEME 2

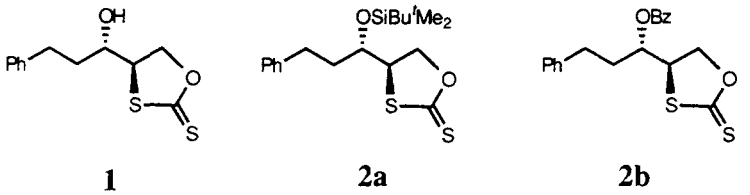
When cyclic xanthate **2a** [7] was treated with tributyltin hydride in refluxing benzene in the presence of a catalytic amount of AIBN, alkene **3a** was obtained in 67% yield. The benzoate **2b**, derived from **1** [8] by the action of benzoyl chloride, also gave the corresponding alkene **3b** in 75% yield under the same conditions. On the other hand, cyclic xanthate **1**, bearing an unprotected secondary alcohol group, gave, on treatment with tributyltin hydride, a complex result. The alkene that had been formed was derivatized and identified by spectroscopic analyses and independent syntheses, as shown in Scheme 4. In one of the independent syntheses, treatment of 3-phenylpropanal with vinylmagnesium bromide gave the expected allylic alcohol [9], which was silylated with *tert*-butyldimethylsilyl chloride to give **3a** in 76% yield. In another independent synthesis, acylation of the allylic alcohol with benzoyl chloride afforded benzoate **3b** in 85% yield. These synthetic materials were identical with those obtained from the tin hydride reaction, after derivatization procedures with the same reagents had been applied to the product.

In considering the reaction mechanism, the stannylthio-substituted carbo radical **I** formed initially by the attack of tributylstannyl radical on **2** undergoes a bond cleavage, not at the O–C bond but at the C–S bond. As the result, the alkanyl radical **II** is produced. It is reasonable that the more stable secondary radical was formed rather than the alternative primary radical that would have resulted from cleavage of the O–C bond, giving an intermediate that would have provided the alkene in a straightforward manner. Alternatively, the radical **II** could have been reduced by tributyltin hydride to give xanthate **III**, which is an appropriate substrate for the Chugaev elimination to afford alkene **3** (R–H) [10]. In order to determine if this was the reaction pathway, tributyltin deuteride was used instead of the tin hydride. If the latter path were taken, the radical intermediate **II** would be reduced by tributyltin deuteride to give the deuterated xanthate **III**. Then the subsequent pyrolytic elimination would have given an alkene, half of which would possess deuterium at the C-2 position of the double bond. However, no deuterated alkene was obtained from the reaction of **2a** with tributyltin deuteride and AIBN. This result indicated that alkene formation actually took place via the β-[(tributylstannylthio)-thiono]oxy alkanyl radical **II** that gave an alkene by a homolytic cleavage of the C–O bond. Alkene formation from β-phenylthio, β-phenylsulfonyl, and β-[(methylthio)-thiono]oxy alkanyl radicals, as depicted in Figure 1, has been reported in the literature [11,12]. These types of radicals produced alkenes through essentially the same reaction mechanism. However, a β-(tributylstannylthio)carboxy alkanyl radical, presumably produced by a tin hydride reaction involving a 1,3-dioxolane-2-thione, actually gave an alkane, as shown in Scheme 6, in which the typical deoxygenation process occurred at the secondary carbon center [13]. The difference between the reactions of 1,3-oxathiolane-2-thione and 1,3-dioxolane-2-thione would be due to an excellent ability of the [(stannylthio)thiono]oxy group but an unfavorable ability of the (stanylthio)carboxy group to undergo the β-elimination step.

The preceding reductions were carried out with use of a 0.01–0.03 M concentration of tributyltin hydride in refluxing benzene. With these concentrations, none of the 1,3-oxathiolane was produced even with use of 3–5 equivalents of tributyltin hydride per 1 equivalent of the 1,3-oxathiolane-2-thione. However, when the reaction was employed with higher concentrations of tributyltin hydride, formation of the 1,3-oxathiolane was observed along with the alkene. The results for reactions of **2b** with tributyltin hydride at different concentrations are listed in Table 1. At lower concentration (below 0.025 M), alkene **3b** was formed exclusively. On the other hand, with a 0.25 M concentration, which was 10 times higher than the former concentration, only 1,3-oxathiolane **4b** was obtained in the reaction. At concentrations of the tin hydride between 0.025 and 0.25 M, it was found that formation of the 1,3-oxathiolane was increased and that of the alkene was decreased as the concentration of the tinhydride was increased. The same correlations were also ob-

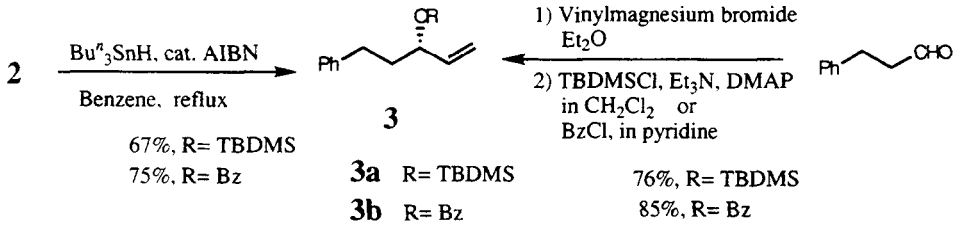


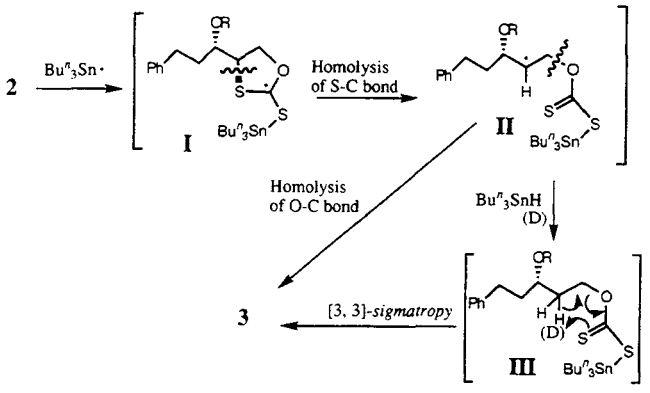
SCHEME 3



1 **2a** **2b**

SCHEME 4





SCHEME 5

TABLE 1 Effects of Bu^n_3SnH Concentration in the Radical Reaction of **2b**

Bu^n_3SnH[a] (*M*)	*Products (% Ratio)*	
	3b	**4b**
0.025	100	0
0.035	94	6
0.05	74	26
0.15	35	65
0.25	0	100

[a] 2.5 equivalents of tributyltin hydride were used.

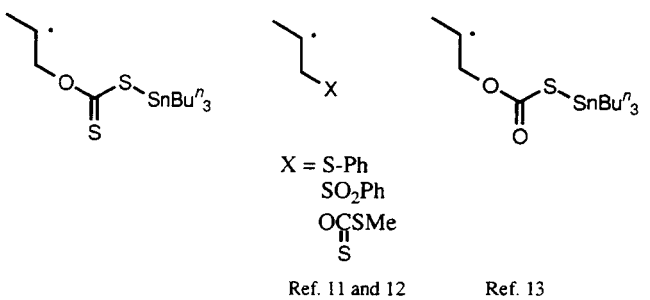
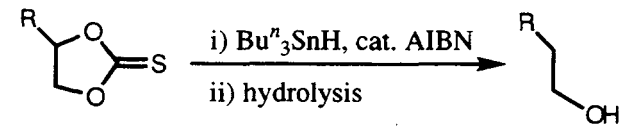


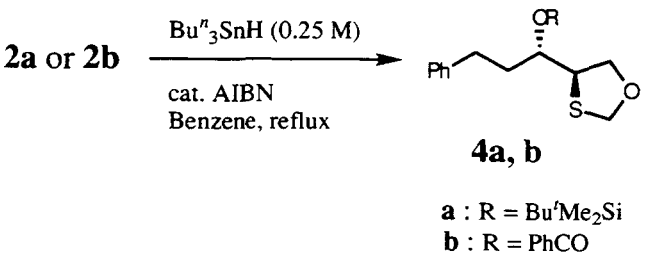
FIGURE 1



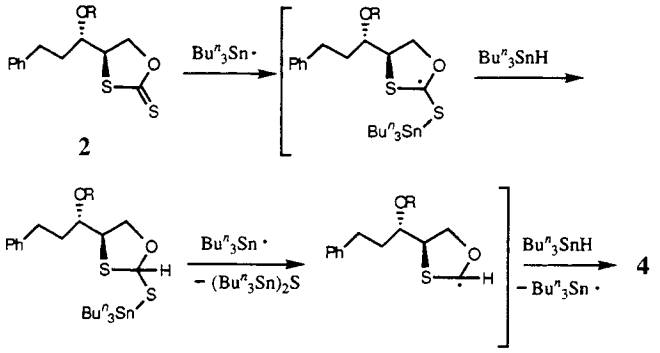
SCHEME 6

served in the cases of alkene **3a** and 1,3-oxathiolane **4a** preparations.

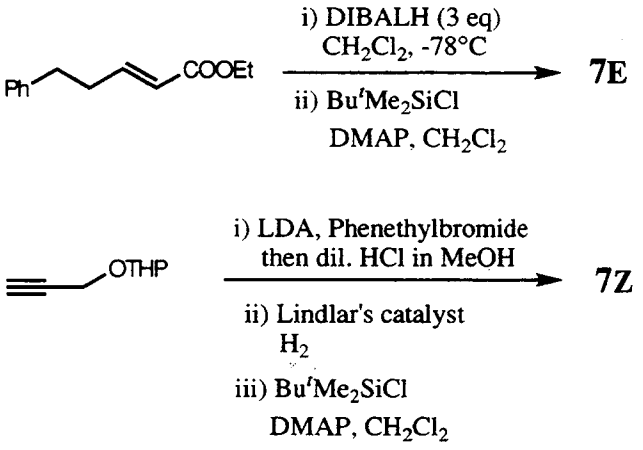
The formation of the 1,3-oxathiolane would be explained by the mechanism shown in Scheme 8. First, the same initial radical is reduced by another tributyltin hydride molecule before C–S bond cleavage occurs at the β-position, and 2-tributylstannylthio-1,3-oxathiolane is produced. Subsequently, an attack by the tributylstannyl radical on the tributylstannyl sulfide moiety may eliminate di(tributylstannyl) sulfide to generate the 1,3-oxathiolanyl radical, which is then reduced by tributyltin hydride to form alkane **4**. The tributyltin



SCHEME 7



SCHEME 8



SCHEME 9

radical formed in the last step is used again for initial attack on the thione. The rate-determining step would probably be formation of the tributylstannylthio-1,3-oxathiolane. The presence of an excess of tributyltin hydride at high concentrations reduces the 2-(tributylstannylthio)-1,3-oxathiolanyl radical before C–S bond cleavage occurs and gives the 1,3-oxathiolane. However, when the concentration of tributyltin hydride is lower than 0.025 M, the C–S bond cleavage may be much faster than the reduction by tributyltin hydride and the alkene results.

Next, reactions of 4,5-disubstituted 1,3-oxathiolane-2-thiones, **5** and **6**, were examined for alkene formation. In these cases, *E* and *Z* olefins are possible products. When the *trans* isomer **5** was heated in a 0.025 M benzene solution of tributyltin hydride with a catalytic amount of AIBN, a mixture of alkenes, **7E** and **7Z**, was formed. They were not readily separable, but their ratio was identified to be 7:1 by proton NMR spectroscopy. On the other hand, a reaction of the *cis* isomer **6** gave a mixture of **7E** and **7Z** in a 4.3:1 ratio. It is noteworthy that the *E* olefin was also produced preferentially in this case. These results indicate that alkene formation is not stereospecific but is stereoselective.

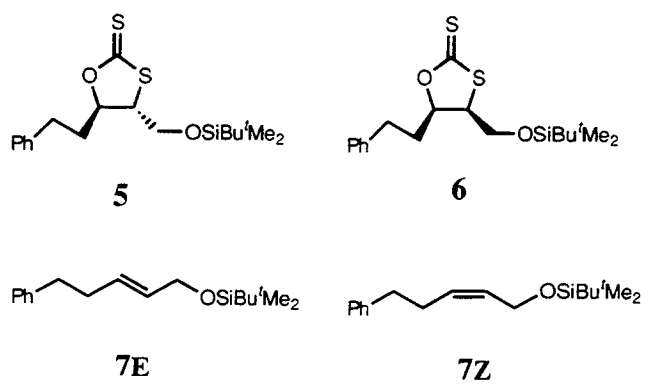


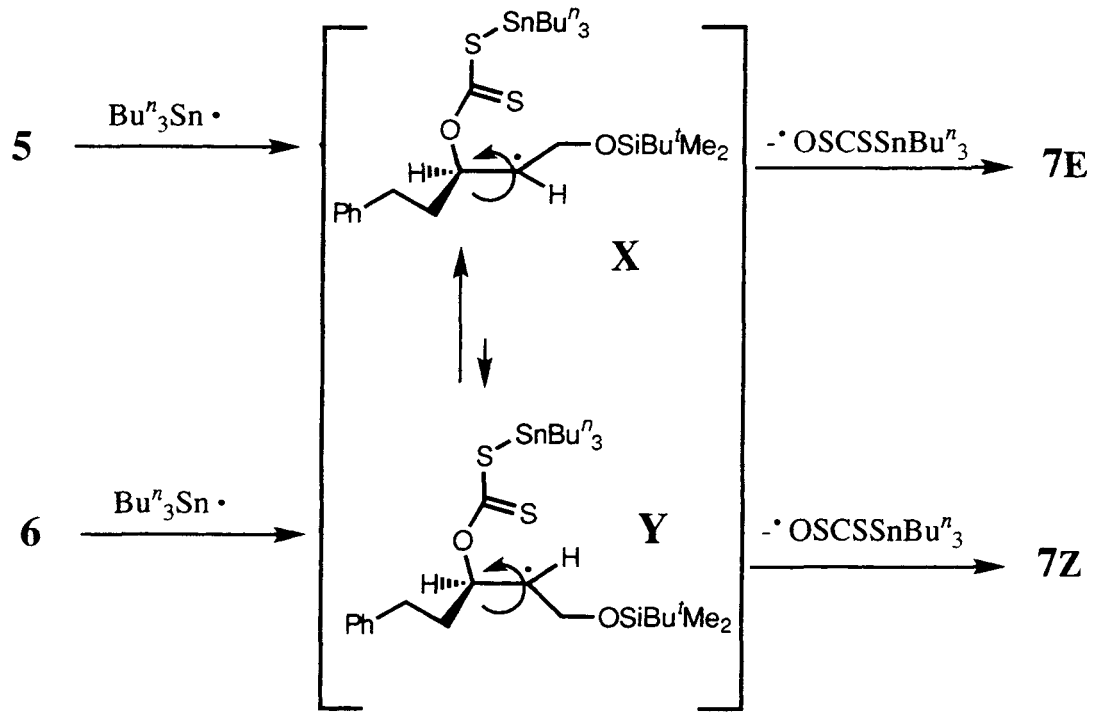
FIGURE 2

The two isomers were identified by independent syntheses. The isomer **7E** was prepared in two steps from (*E*)-ethyl 5-phenyl-2-pentenoate [14]. Thus, DIBALH reduction of the unsaturated ester to (*E*)-5-phenyl-2-pentenol, followed by silylation with tert-butyldimethylsilyl chloride, gave **7E** as a pure geometric form in 75% yield. Compound **7Z** was obtained by a four-step procedure from the THP ether of propargyl alcohol. Alkylation of the lithium salt of the terminal acetylene moiety of the protected propargyl alcohol with 2-phenylethyl bromide in HMPA, followed by acidic deprotection of the THP ether, gave 5-phenyl-2-pentyn-1-ol. *Cis* selective reduction of the triple bond by Lindlar's catalyst under a hydrogen atmosphere, and silylation of the resulting *cis* allylic alcohol with *tert*-butyldimethylsilyl chloride, afforded **7Z** in 10% yield with excellent geometrical purity.

Although the mechanisms of these reactions were not fully explainable by the evidence presented here, at this point, we can at least make an attempt to explain the results, as shown in Scheme 10. The lifetime and stability of the intermediary radical would influence the selectivity. As we have shown in Scheme 5, the intermediate radical **X** is produced initially from the *trans* 1,3-oxathiolane-2-thione **5**, and it subsequently eliminates a xanthate radical to lead to the *E* alkene **7E**. On the assumption that some of **X** rotate to the alternative conformer **Y**, this can lead to the *Z* alkene, **7Z**. On the other hand, the radical **Y** derived form *cis* isomer **6**, will afford same **7Z**, but mainly will give **7E** through formation of the more stable conformer **X** in a fast equilibration before formation of **7Z**.

Transformation of Geraniol to Linalool Silyl Ether

Finally, the alkene formation reaction was applied to the preparation of linalool. The epoxy alcohol **8**



SCHEME 10

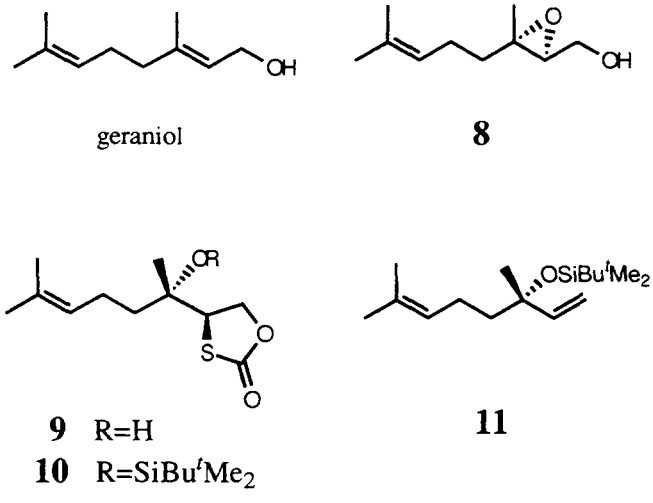


FIGURE 3

was obtained from geraniol by the Sharpless asymmetric oxidation [15]. By the same procedure reported previously [8], treatment of **8** with carbon disulfide in the presence of potassium hydride gave **9** in 53% yield. Silylation of the tertiary alcohol group of **9** with *tert*-butyldimethylsilyl trifluoromethanesulfonate in the presence of 2,6-lutidine gave the silyl ether **10** in 86% yield. Compound **10** was subjected to the tributyltin hydride reaction in 0.025 M benzene solution in the presence of a catalytic amount of AIBN at 85°C to give (+)-linalool silyl ether **11** in 73% yield.

CONCLUSIONS

We have found that a 1,3-oxathiolane-2-thione reacts with tributyltin hydride in the presence of AIBN to form an alkene and/or a 1,3-oxathiolane. At a low concentration of tributyltin hydride, the alkene is produced predominantly, while reduction of the thione group to a methylene group occurred at higher concentration of tributyltin hydride. The tributyltin radical promoted reactions of *cis*- and *trans*-4,5-dialkyl substituted 1,3-oxathiolane-2-thiones take place stereoselectively to give the *E* alkene preferentially.

EXPERIMENTAL

Melting points were taken on a Yanako micro-melting apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on JEOL GXS and Varian Gemini 300 spectrometers for ^{1}H (400 or 300 MHz) and for ^{13}C (100 or 75 MHz). The chemical shifts were shown as δ-values using tetramethylsilane (0 ppm) for proton spectra and $CDCl_3$ (77.0 ppm) for carbon spectra as internal standards. Infrared (IR) spectra were recorded by use of a JASCO IRA-1 spectrometer and were taken as liquid films on NaCl plates or as tablets. Low- and high-resolution mass spectra (LRMS and HRMS) were ob-

tained on a JEOL JMS 303HF spectrometer at the Analytical Center of Okayama University of Science by the electron impact (EI) method at 70 eV unless otherwise stated. Only significant peaks are described here for IR and MS spectra. Silica gel (Merck 7734, 70–300 mesh) was used for gravity column chromatography and silica gel (Merck 9385, 230–400 mesh) for flash column chromatography. Precoated silica gel plates (Merck 5715, 60F254) were used for thin layer chromatography. All air-sensitive reactions were conducted in flame-dried glassware under an Ar atmosphere. THF and ether used as solvents for reactions were dried over sodium benzophenone ketyl, and methylene chloride and carbon disulfide were dried over phosphorus pentoxide. These solvent reagents were freshly distilled just before use.

Alkene Formation at 0.025 M Concentration of Tributyltin Hydride

A mixture of 1,3-oxathiolane-2-thione (0.3 mmole) and AIBN (0.015 mmole) was dissolved in a degassed 0.025 M benzene solution (20 mL) of tributyltin hydride, and the solution was refluxed for 5–30 minutes. After cooling, the mixture was diluted with benzene (40 mL) and washed with aq. $NaHCO_3$ (4 mL), water (4 mL), and brine (4 mL). The organic layer was dried over $MgSO_4$ and evaporated. The residual oil was purified by column chromatography on silica gel. Eluent, yield, physical, and spectroscopic data are described as follows.

3a: Oil, yield 67%. Eluent for chromatography, 5% ethyl acetate in hexane. *Rf* = 0.50 (5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 7.28–7.22 (2H, m), 7.13–7.08 (3H, m), 5.80 (1H, ddd, *J* = 16.9, 10.3, and 5.9 Hz), 5.14 (1H, ddd, *J* = 16.9, 1.5, and 1.1 Hz), 5.03 (1H, ddd, *J* = 10.3, 1.5, and 1.1 Hz), 4.12 (1H, dt, *J* = 12.1 and 5.9 Hz), 2.60 (2H, m), 1.74 (2H, m), 0.87 (9H, s), 0.06 (3H, s), 0.02 (3H, s). ^{13}C NMR ($CDCl_3$) δ 142.4, 141.4, 128.4, 128.3, 125.7, 113.9, 73.3, 39.8, 31.5, 25.9, 18.3, −4.3, −4.8. MS (relative intensity) *m/z* 219 (M − 57, 93), 201 (13), 144 (54). HRMS (FAB) Anal. calcd for $C_{17}H_{29}OSi$: 277.1988 (M + 1). Found: 277.1980.

3b: Oil, yield 75%. Eluent for chromatography, 5% ethyl acetate in hexane. *Rf* = 0.35 (10% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 78.06 (2H, m), 7.356 (1H, m), 7.47–7.42 (2H, m), 7.30–7.24 (2H, m), 7.21–7.15 (3H, m), 5.93 (1H, ddd, *J* = 16.9, 10.6, and 6.2 Hz), 5.53 (1H, dt, *J* = 12.8 and 6.2 Hz), 5.34 (1H, dm, *J* = 16.9 Hz), 5.24 (1H, dd, *J* = 10.6 and 1.1 Hz), 2.82–2.68 (2H, m), 2.20–2.00 (2H, m). ^{13}C NMR ($CDCl_3$) δ 165.6, 141.2, 136.2, 132.8, 130.3, 129.5, 128.3, 128.2, 125.9, 116.8, 74.6, 35.8, 31.3. IR (film) 1720 cm^{-1}. MS (relative intensity) *m/z* 144 (M − 121, base), 143 (20), 129 (80). HRMS (FAB) Anal. calcd for $C_{18}H_{29}O_2$: 267.1385 (M + 1). Found: 267.1395.

The yields of the reaction with **5** and **6** were 79 and 70%, respectively. The following data for **7E** and **7Z** were obtained by independent syntheses, and those experiments will be described later.

7E: Oil. Eluent for chromatography, 5% ethyl acetate in hexane. *Rf* = 0.30 (2.5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 7.30–7.23 (2H, m), 7.20–7.13 (3H, m), 5.69 (1H, m), 5.54 (1H, m), 4.09 (2H, dd, *J* = 5.1, and 1.5 Hz), 2.70–2.64 (2H, m), 2.38–2.30 (2H, m), 0.89 (9H, s), 0.04 (6H, s). ^{13}C NMR ($CDCl_3$) δ 141.8, 130.2, 129.8, 128.4, 128.2, 125.7, 63.9, 35.6, 34.0, 26.0, 18.4, −5.2. MS (relative intensity) *m/z* 219 (M − 57, 61), 201 (8), 189 (25), 144 (16), 143 (22), 75 (base). HRMS (FAB) Anal. calcd for $C_{17}H_{28}OSi$: 277.1988 (M + 1). Found: 277.1989.

7Z: Oil. Eluent for chromatography, 5% ethyl acetate in hexane. *Rf* = 0.25 (2.5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 7.27–7.20 (2H, m), 7.17–7.10 (3H, m), 5.53–5.38 (2H, m), 4.08 (2H, d, *J* = 5.8 Hz), 2.63 (2H, t, *J* = 8.1 Hz), 2.31 (2H, dt, *J* = 8.1 and 7.0 Hz), 0.83 (9H, s), 0.03 (6H, s). ^{13}C NMR ($CDCl_3$) δ 141.9, 130.3, 129.5, 128.4, 128.3, 125.9, 59.3, 35.8, 29.5, 26.0, 18.4, −5.1. MS (relative intensity) *m/z* 219 (M − 57, 64), 201 (9), 189 (16), 144 (10), 143 (20), 75 (base). HRMS (FAB) Anal. calcd for $C_{17}H_{28}OSi$: 277.1988 (M + 1). Found: 277.1997.

Alternative Syntheses of **3a** *and* **3b**. To a THF solution (10 mL) of 3-phenylpropanal (3 mmole) was added vinylmagnesium bromide (3.5 mL, 1 M solution in ether) at 0°C, and the mixture was stirred for 20 minutes at room temperature. Saturated ammonium chloride (10 mL) was added to the mixture and it was extracted with ether (80 mL). The ethereal extract was washed with water (4 mL) and brine (4 mL) and dried over $MgSO_4$. Removal of solvent gave a crude allylic alcohol quantitatively, which was identified by proton NMR spectra given in the literature [9]. The crude material was used directly for the next steps. The crude allylic alcohol (1 mmole) was dissolved in methylene chloride (2 mL), and *tert*-butyldimethylsilyl chloride (1.3 mmole), DMAP (0.6 mmole), and triethylamine (2 mmole) were added to the solution; this was stirred for 4 hours at room temperature. The solution was treated with water (30 mL) and extracted with benzene (100 mL). The organic layer was washed with water (7 mL × 2), and brine (7 mL) and dried over $MgSO_4$. The solvent was evaporated, and the residual oil was purified by column chromatography on silica gel to give pure **3a** in 92% yield.

To the crude allylic alcohol (1 mmole) in pyridine (2 mL) was added benzoyl chloride (1.2 mmole) at room temperature. After the solution had been stirred for 20 minutes, it was diluted with ether (100 mL) and washed with water (6 mL × 3) and brine (6 mL). The extract was dried over $MgSO_4$ and concentrated under reduced pressure. The re-

sidual oil was purified by column chromatography on silica gel to give **3b** in 90% yield.

Alternative Synthesis of **7E**. To a methylene chloride solution (60 mL) of ethyl 5-phenyl-2-pentenoate (1 mmole) [14] was added dropwise DIBALH (3 mL, 1.0 M hexane solution) at −78°C. The solution was stirred for 1 hour at −78°C and then allowed to warm to room temperature. The mixture was treated with dil. HCl (15 mL), and the organic layer was washed with water (5 mL) and brine (5 mL). The extract was dried over $MgSO_4$ and evaporated to give the crude allylic alcohol. To the crude alcohol dissolved in dry methylene chloride (3 mL) were added *tert*-butyldimethylsilyl chloride (1.1 mmole) and DMAP (1 mmole), and the solution was stirred for 2 hours at room temperature. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with water (5 mL × 3) and brine (4 mL). The extract was dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel using 5% ethyl acetate in hexane as an eluent to give oily **7E** in 67% yield.

Alternative Synthesis of **7Z**. To a THP ether of propargyl alcohol (4 mmole) in anhydrous THF (4 mL) was added dropwise butyllithium (2.67 mL, 1.61 M in hexane solution) at room temperature during 15 minutes. The mixture was stirred for a further 15 minutes. Then, HMPA (0.3 mL) was added, and the solution was warmed to 40°C. An HMPA solution (0.4 mL) of 2-phenylethyl bromide (4 mmole) was added in three portions at the same temperature, and the mixture was allowed to stir for 20 hours. The mixture was diluted with ether (80 mL) and washed with water (5 mL × 3) and brine (5 mL). The ethereal extract was dried over $MgSO_4$ and evaporated. The crude product was then hydrolyzed with *c*-HCl (0.1 mL) in methanol (3 mL) at room temperature for 10 minutes. The reaction mixture was neutralized with triethylamine, and the whole was concentrated under reduced pressure. The residue was extracted with ethyl acetate (50 mL) and washed with water (4 mL × 3) and brine (4 mL). The extract was dried over $MgSO_4$ and evaporated. The residual oil was purified by column chromatography on silica gel and eluted with 30% ethyl acetate in hexane to afford 5-phenyl-3-pentyn-1-ol in 18% yield. *Rf* = 0.25 (double development by 5% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$) δ 7.33 (5H, m), 4.23 (2H, dt, *J* = 5.9 and 2.2 Hz), 2.83 (2H, t, *J* = 7.5 Hz), 2.52 (2H, tt, *J* = 7.5 and 2.2 Hz), 1.54 (1H, t, *J* = 5.9 Hz). A mixture of the pentynyl alcohol (0.6 mmole) and Lindlar's catalyst (25 mg, purchased from Aldrich Co.) in methylene chloride (0.3 mL) was stirred under a hydrogen atmosphere. After stirring for 3 hours, the catalyst was filtered off and the filtrate was evaporated. The oily residue was silylated with *tert*-butyldimethylsilyl chloride under the same conditions described for **7E** to give the desired **7Z** in 58% yield.

General 1,3-Oxathiolane Preparation with the 0.25 M Concentration of Tributyltin Hydride

A mixture of 1,3-oxathiolane-2-thione (3 mmole) and AIBN (0.015 mmole) was dissolved in a degassed 0.25 M benzene solution (3 mL) of tributyltin hydride, and the solution was refluxed for 10–15 minutes. The same workup as in the case of the 0.025 M concentration reaction and subsequent purification gave the 1,3-oxathiolane.

4a: Oil, yield 70%. Eluent for chromatography, 5% ethyl acetate in hexane. *Rf* = 0.58 (7.5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 7.29–7.23 (2H, m), 7.18–7.14 (3H, m), 4.93 (1H, d, *J* = 5.1 Hz), 4.82 (1H, d, *J* = 5.1 Hz), 4.05 (1H, dd, *J* = 9.5 and 4.0 Hz), 3.89 (1H, dd, *J* = 9.5 and 5.9 Hz), 3.74 (1H, ddd, *J* = 8.8, 4.0, and 4.0 Hz), 3.61 (1H, ddd, *J* = 8.8, 5.9, and 4.0 Hz), 2.72–2.62 (2H, m), 1.99–1.81 (2H, m), 0.94 (9H, s), 0.06 (3H, s) 0.04 (3H, s). ^{13}C NMR ($CDCl_3$) δ 142.3, 128.4, 128.3, 125.8, 74.1, 73.8, 72.8, 52.8, 37.4, 29.9, 25.9, 18.1, −4.0, −4.6. MS (relative intensity) *m/z* 339 (M + 1). MS (FAB) *m/z* 281 (M − 57, base), 249 (23), 233 (7), 189 (5), 77 (31). HRMS (FAB) Anal. calcd for $C_{18}H_{31}O_2SSi$: 339.1814 (M + 1). Found: 339.1801.

4b: Oil, yield 78%. Eluent for chromatography, 20% ethyl acetate in hexane. *Rf* = 0.40 (5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 8.00–7.95 (2H, m), 7.50 (1H, m), 7.42–7.35 (2H, m), 7.20–7.15 (2H, m), 7.12–7.05 (3H, m), 5.16 (1H, td, *J* = 7.7, and 4.0 Hz), 4.87 (1H, d, *J* = 5.5 Hz), 4.74 (1H, d, *J* = 5.1 Hz), 3.95 (1H, dd, *J* = 9.5 and 3.7 Hz), 3.83–3.70 (2H, m), 2.63 (2H, m), 2.10–2.00 (2H, m). ^{13}C NMR ($CDCl_3$) δ 165.9, 141.2, 133.2, 129.9, 129.7, 128.4, 128.4, 128.3, 126.0, 75.4, 73.4, 72.8, 51.6, 34.5, 31.5. IR (film) 1718 cm^{-1}. MS (relative intensity) *m/z* 207 (M − 121, 17), 206 (90), 149 (35), 105 (base). HRMS (FAB) Anal. calcd for $C_{19}H_{21}O_3S$: 329.1212 (M + 1). Found: 329.1203.

Preparation of Substrates **2a** *and* **6**

The compounds **2a** and **6** were prepared from the corresponding alcohols [7,8] by silylation, as follows. To a stirred methylene chloride solution (20 mL) of alcohol (2 mmole) and 2,6-lutidine (8 mmole) was added, dropwise, *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.4 mmole) at room temperature during 5 minutes. The mixture was stirred for 20 minutes and washed with water (2 mL × 2) and brine (2 mL). The organic layer was dried over $MgSO_4$ and evaporated. The residual oil was purified by chromatography on silica gel.

2a: Colorless crystals, mp 95–97°C recrystallized from hexane, 87% yield. Eluent for chromatography, 10% ethyl acetate in hexane. *Rf* = 0.40

(20% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 8.06–8.01 (2H, m), 7.63 (1H, m), 7.51–7.45 (2H, m), 7.30–7.24 (2H, m), 7.22–7.13 (3H, m), 5.37 (1H, ddd, J = 9.5, 6.2, and 3.7 Hz), 4.90 (1H, dd, J = 10.3 and 4.4 Hz), 4.85 (1H, dd, J = 10.3 and 6.6 Hz), 4.32 (1H, m ddd, J = 6.6, 6.2, and 4.4 Hz), 2.80–2.65 (2H, m), 2.28–2.19 (1H, m), 2.13–2.01 (1H, m), 1.70 (1H, broad). ^{13}C NMR ($CDCl_3$) δ 210.3, 165.7, 140.1, 133.7, 129.8, 129.0, 128.7, 128.6, 128.3, 126.4, 78.4, 73.1, 54.0, 33.2, 31.4. IR (KBr) 1720, 1160 cm^{-1}. MS (FAB) m/z 359 (M + 1). HRMS (FAB) Anal. calcd for $C_{19}H_{19}O_3S_2$: 359.0776 (M + 1). Found: 359.0798. Anal. calcd for $C_{19}H_{18}O_3S_2$: C, 63.66; H, 5.06. Found: C, 64.01; H, 5.30.

6: Oil, yield 77%. Eluent for chromatography, 2.5% ethyl acetate in hexane. Rf = 0.59 (double development by 5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 7.34–7.21 (5H, m), 5.00 (1H, ddd, J = 9.9, 5.1, and 4.0 Hz), 3.88–3.77 (3H, m), 3.00 (1H, ddd, J = 14.7, 9.2, and 5.1 Hz), 2.81 (1H, ddd, J = 14.7, 8.8, and 5.1 Hz), 2.40 (1H, ddt, J = 14.3, 8.8, and 5.1 Hz), 2.10 (1H, dddd, J = 14.9, 9.2, 5.1, and 4.0 Hz), 0.87 (9H, s), 0.06 (6H, s). ^{13}C NMR ($CDCl_3$) δ 140.1, 128.7, 128.5, 128.3, 126.4, 96.1, 91.6, 61.4, 55.4, 32.6, 31.4, 25.7, 18.1, −5.5, −5.6. IR (film) 1160 cm^{-1}. MS (relative intensity) m/z 311 (M − 57, 21), 281 (7), 251 (54), 219 (76), 75 (base). MS (FAB) m/z 369 (M + 1). HRMS (FAB) Anal. calcd for $C_{18}H_{29}O_2S_2Si$: 369.1378 (M + 1). Found: 369.1402.

Synthesis of Linalool Silyl Ether

Preparation of **9**. This compound was obtained in 53% yield from geraniol *mono* epoxide [15] by the same protocol described in our previous report [8]. Oil. Eluent for chromatography, 20% ethyl acetate in hexane Rf = 0.35 (20% ethyl acetate in hexane). $[\alpha]_{D^{25}}$ −40.6 (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ 5.14–5.07 (2H, m), 4.85 (1H, dd, J = 10.3, and 7.3 Hz), 4.05 (1H, dd, J = 7.3, and 3.7 Hz), 2.07–2.01 (2H, m), 1.70 (3H, s), 1.63 (3H, s), 1.61–1.51 (2H, m), 1.29 (3H, s). ^{13}C NMR ($CDCl_3$) δ 123.1, 78.6, 73.5, 60.4, 39.1, 25.5, 23.1, 21.9, 20.9, 17.6, 14.0. IR (neat) 3420, 1200 cm^{-1}. MS (FAB) m/z 247 (M + 1). HRMS (FAB) Anal. calcd for $C_{11}H_{18}O_2S_2$: 247.0827 (M + 1). Found: 247.0845.

Preparation of **10**. The silylation of **9** was performed by the same procedure described for **2a** and **6**. Oil, 86% yield. Eluent for chromatography, 5% ethyl acetate in hexane. Rf = 0.46 (10% ethyl acetate in hexane). $[\alpha]_{D^{25}}$ −16.4 (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ 5.04–4.96 (2H, m), 4.80 (1H, m), 4.08 (1H, dd, J = 7.7, and 4.0 Hz), 2.00–1.90 (2H, m), 1.66 (3H, s), 1.57 (3H, s), 1.53–1.44 (2H, m), 1.28 (3H, s), 0.86 (9H, s), 0.14 (3H, s), 0.11 (3H, s). ^{13}C NMR ($CDCl_3$) δ 212.4, 132.5, 123.2, 78.6, 76.5, 59.4, 40.4, 25.7, 25.6, 24.1, 22.3, 18.2, 17.7, −2.0, −2.3. IR (film) 1205 cm^{-1}. MS (FAB) m/z 361 (M + 1). HRMS (FAB) Anal. calcd for $C_{17}H_{33}O_2S_2Si$: 361.1691 (M + 1). Found: 361.1701.

Formation of Alkene **11** *from* **10**. This reaction was carried out under the same reaction conditions as described for typical alkene formation. The alkene **11** was obtained in 73% yield as an oil. Eluent for chromatography, 5% ethyl acetate in hexane. Rf = 0.40 (5% ethyl acetate in hexane). $[\alpha]_{D^{25}}$ +7.1 (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ 5.84 (1H, dd, J = 17.2 and 6.6 Hz), 5.14 (1H, dd, J = 17.2 and 1.5 Hz), 5.09 (1H, tm, J = 7.3 Hz), 4.98 (1H, dd, J = 10.6 and 1.6 Hz), 2.08–1.90 (2H, m), 1.67 (3H, s), 1.59 (3H, s), 1.53–1.45 (2H, m), 1.29 (3H, s), 0.89 (9H, s), 0.07 (3H, s), 0.06 (3H, s). ^{13}C NMR ($CDCl_3$) δ 145.7, 131.1, 124.8, 111.5, 75.5, 43.8, 27.4, 25.9, 25.7, 22.8, 18.3, 17.6, −2.1. MS (FAB) m/z 296 (M + 1). HRMS (FAB) Anal. calcd for $C_{16}H_{33}OS$: 269.2301 (M + 1). Found: 269.2305.

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