Sonochemical Initiation of Radical Chain Reactions. Hydrostannation and Hydroxystannation of C–C Multiple Bonds

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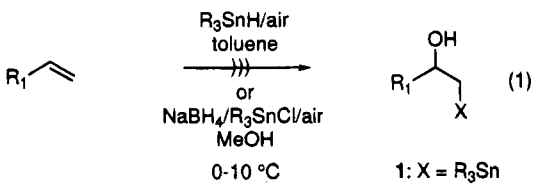
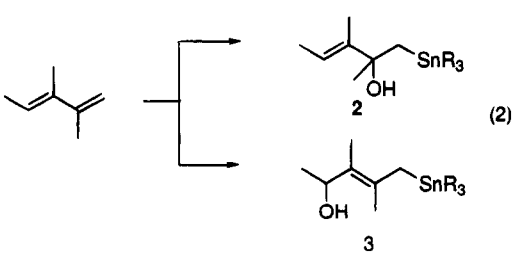
Irradiation of R_3SnH with ultrasound generates tin radicals in the region of hot sonochemical cavities, which then undergo useful synthetic reactions in the bulk liquid phase. Thus, ultrasound irradiation of a mixture of a tin hydride and an alkyne produces vinylstannanes at temperatures as low as −50 °C, and the reactions under irradiation have been found to proceed >100 times faster than those without it. Hydrostannation of electron-deficient olefins also proceeds at low temperatures. Ultrasound-promoted radical reaction of an organotin hydride reagent to an activated olefin in the presence of air results in the addition of stannyl and hydroxyl groups across the C–C double bond (hydroxystannation). The reaction of dienes may proceed either in a 1,2- or 1,4-manner to provide β-hydroxy stannanes or hydroxylated allylic stannanes, respectively. Instead of using a tin hydride reagent, the use of a mixture of a tin chloride reagent and $NaBH_4$ as an in situ source of a tin hydride reagent made an experimentally convenient method for the hydroxystannation reaction.

"Nonhomogeneous" systems are a class of *homogeneous* medium where the local properties are *heterogeneous*:[1] an example may be a solution, wherein the bulk temperature remains constant while the local temperature is either high or low depending on time and location. Such a system has rarely been used intentionally for synthetic purposes, and hence its utility has not yet been explored. We have been interested in such systems for sometime and now describe a use of thermally nonhomogeneous medium to achieve unusual synthetic consequences in radical reactions (hydroxystannation of olefins).[2–4]

Irradiation of homogeneous liquid with ultrasound produces characteristic thermal nonequilibrium conditions by creating localized superheated sonochemical cavities, wherein a maximum temperature over 2000 K can be generated.[5] It is commonly accepted that the unusual observations made in the ultrasound-driven chemical reactions are largely due to this acoustic cavitation. In contrast to heterogeneous sonochemistry, which has been widely employed in organic synthesis,[6–8] organic sonochemistry in homogeneous media (i.e., under nonhomogeneous environment, vide supra)[9] has not been explored.[10] This may be due in part to poor efficiency of acoustic cavitation in homogeneous liquid phase and in part to the fact that the cavities themselves are too small in size (diameter of <1 μm) and too short-lived (<2 μs) to serve as a medium for product formation on a synthetically useful scale.[2]

In this article, we show that homogeneous sonochemistry at low temperatures allows the tin radical species[11,12] to react in a previously unknown manner. Thus, when an aerated solution of R_3SnH and an olefin is irradiated at 0 to 10 °C, *hydroxy*stannation rather than the conventional hydrostannation of the C–C double bond takes place to produce a hydroxy stannane (**1**, eq 1, X = R_3Sn). The hydroxystannation of 1,3-dienes may





proceed either in a 1,2- or 1,4-manner[13] to provide β-hydroxy stannanes **2** or hydroxylated allylic stannanes

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(1) Cf. Freeman, G. R., Ed. *Kinetics of Nonhomogeneous Processes*; John Wiley: New York, 1987.

(2) For a preliminary communication on the hydrostannation section of this article; see: Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849.

(3) Kawashima, E.; Aoyama, Y.; Sekine, T.; Nakamura, E.; Kainosho, M.; Kyogoku, Y.; Ishido, Y. *Tetrahedron Lett.* **1993**, *34*, 1317.

(4) Nakamura, E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.* **1991**, *112*, 8980.

(5) (a) Cf. Suslick, K. S.; Hammerton, D. A.; Cline, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5641. (b) Reviews: Ley, S. V.; Low, C. M. R. *Ultrasound in Synthesis*; Springer: Berlin, 1989. Mason, T. J. *Chemistry with Ultrasound;* Elsevier Applied Science: London, 1990.

(6) The efficiency of acoustic cavitation becomes higher in the presence of a solution/solid interface, and hence, even a weak source of ultrasound (i.e., an ultrasound cleaner) is effective in heterogeneous sonochemistry.

(7) Luche, J. L.; Damiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7926.

(8) (a) Renaud, P. *Bull. Chim. Soc. Fr. Ser. S.* **1950**, *17*, 1044. Fry, A. J.; Herr, D. *Tetrahedron Lett.* **1978**, 1721. de Souza-Barboza, J. C.; Petrier, C.; Luche, J. L. *J. Org. Chem.* **1988**, *53*, 1212. (b) Reviews: Kimura, T.; Ando, T. *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Soc. Jpn.)* **1988**, *46*, 1124. Lindley, J.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 275. Abdulla, R. F. *Aldrichimica Acta* **1988**, *21*, 31. Moon, S. *CHEMTECH* **1987**, 434. Boudjouk, P. *J. Chem. Educ.* **1986**, *63*, 427. Mason, T. J. *Ultrasonics* **1986**, *24*, 245.

(9) (a) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73. Suslick, K. S. *Mod. Synth. Methods* **1986**, *4*, 1. (b) Lorimer, J. P.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 239.

(10) Cf. Suslick, K. S.; Schubert, P. F.; Goodale, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 7342. Suslick, K. S.; Goodale, J. W.; Schubert, P. F.; Wang, H. H. *Ibid.* **1983**, *105*, 5781. See also: Brown, H. C.; Racherla, U. S. *Tetrahedron Lett.* **1985**, *27*, 2187. Menéndez, J. C.; Trigo, G. G.; Söllhuber, M. M. *Tetrahedron Lett.* **1986**, *27*, 3285. Kruus, P.; Patraboy, T. J. *J. Phys. Chem.* **1985**, *89*, 3379. Lee, J.; Snyder, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 1522.

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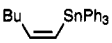
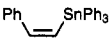
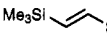
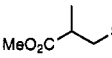
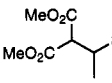
Table 1. Sonochemical Hydrostannation with Ph_3SnH[a]

			sonochemical				control	
entry	substrate (equiv)	solvent	time (h)	temp (°C)	% yield[b] (% cis)[c]	major product	temp (°C)	% yield[d]
1	 (5)	none	3	7	95(92)		0	1
2		toluene[e]	2	7	86(91)		7	3
3		THF	0.25	7	72(93)			
4	 (3)	toluene	2.5	6	83(73)		7	13[c]
5			4	−8	50(92)			
6			13	−50	40(nd)			
7		THF[e]	1.5	−55	61(87)			
8	 (3)	toluene	5	−8	78(8)		0	0
9		THF[e]	8	−55	39[g,f] (17)		−70	<1
10	 (2)	Toluene[e]	2.5	6	94		8	<2
11	 (2)	toluene	5	7	63		0	<1
12	 (0.67)	toluene	8	8	39		0	6

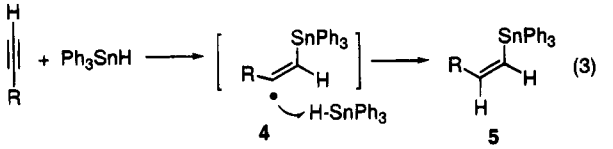
[a] The reaction was carried out in a 0.5 M solution except in entry 2 where a 0.25 M solution was used. In low-yield runs, good material balance was observed. [b] Isolated yield except in entries 2 and 3 where GLC yields are reported. [c] Determined by GLC except in entries 4 and 5 where the ratio was determined by ^{13}C NMR. nd = not determined. [d] Determined by NMR or GLC. [e] With AIBN (10 mol %). [f] Ca. 10% of Ph_3SnH was recovered.

3 (eq 2), respectively. These transformations indicate that, at low temperatures, tin radicals are compatible with molecular oxygen, to which they are intrinsically reactive. Addition of two heteroatoms across an olefinic bond (eq 1) is an important class of synthetic transformations as represented by the classical halohydrin formation and oxymercuration reaction (X = halogen or Hg(II) for **1**).[14,15] The "Hydroxystannation" reaction provides the first access to hydroxylated organotin compounds through addition of stannyl and hydroxyl groups to an olefin.

In order to put these results into perspective, we first summarize the sonochemical generation of tin radical species in the reaction of R_3SnH with a C−C multiple bond *under argon*[9] and then detail the new reaction that takes place *in the presence of air*.

Results and Discussion

Homogeneous Sonochemistry of Hydrostannation. Addition of a tin hydride reagent to an acetylene is a useful synthetic reaction (eq 3),[16] representing the simplest member of radical chain reactions involving turnover of a tin radical species. Straightforward reaction mechanism and sensitivity of product stereochemistry to the reaction conditions made this reaction a useful probe to examine the effects of ultrasound irradiation on a radical chain reaction. The reaction is normally carried out by heating a neat mixture of a tin hydride and an acetylene in the presence of AIBN to obtain a vinylstannane (**5**) in high yield. We found that sonochemical irradiation dramatically accelerates this reaction.



Taking the reaction of 1-hexyne (5 equiv) with Ph_3SnH under argon as a test reaction, we investigated the product yield and the cis/trans isomer ratio against variation of the reaction conditions (e.g., on/off of ultrasound, temperature, and solvent). Under the usual thermal conditions, the reaction of a neat mixture of two reactants proceeded at 90 °C and gave a 100% yield. The reaction was extremely slow in an ice bath (1% yield at 0 °C, 3 h). However, when the reaction mixture was sonicated for 3 h under argon with a titanium immersion horn (see Experimental Section), 1-(triphenylstannyl)hex-1-ene formed in 88% isolated yield predominantly (92%) as the cis isomer (Table 1, entry 1). During this experiment, the internal temperature rose slightly after a few minutes and remained constant (7 °C) throughout the reaction period. The sonochemical reaction proceeded equally well in toluene at 7 °C (entry 2, 86% yield, 91%

(11) According to recent classification of sonochemistry by Luche, radical chain reaction is an ideal target of sonochemical activation: Luche, J. L.; Einhorn, C.; Einhorn, J. *Tetrahedron Lett.* **1990**, *31*, 4125.

(12) Cf. ESR detection of radical species upon thermolysis of R_4Sn and ditins: Rehorek, D.; Janzen, E. G. *J. Organomet. Chem.* **1984**, *268*, 135.

(13) For the rich chemistry of palladium-catalyzed 1,4-difunctionalization of dienes, see: Bäckvall, J. E.; Andersson, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 6374 and references therein.

(14) (a) Block, E.; Schwan, A. L. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, Chapter 1.8. (b) Radical variants of this transformation are rare: Curran, D. P. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.: Pergamon: Oxford, 1991; Vol. 4, pp 770−771.

(15) A rare radical variation to simultaneously add sulfur and oxygen atoms: Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099.

(16) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47. van der Kerk, G. J. M.; Noltes, J. G. *Ibid.* **1959**, *9*, 106. Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. Leusink, A. J.; Budding, H. A.; Drenth, W. *Ibid.* **1967**, *9*, 295.

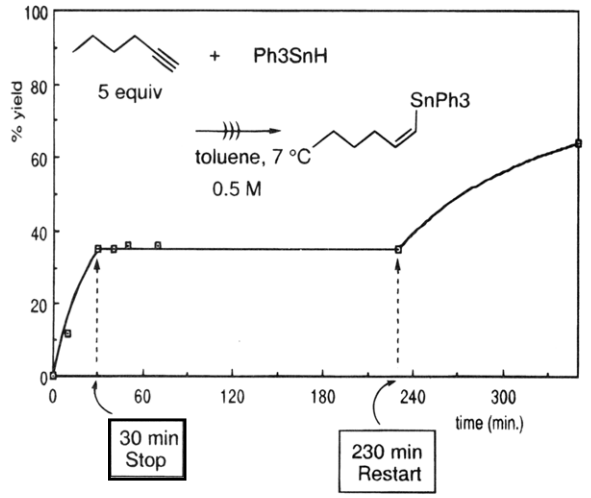


Figure 1. Progress of the hydrostannation reaction (eq 3) with and without ultrasound irradiation.

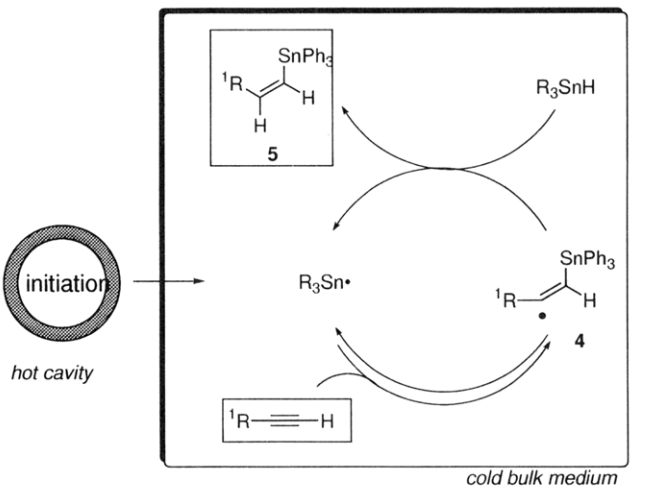
cis, 2 h), whereas the reaction without irradiation proceeded only to 3% conversion. No induction time was observed in the sonochemical reaction, and the reaction took place only during ultrasound irradiation, without which the reaction almost completely stopped (Figure 1). The sonochemical reaction does not necessarily need a radical initiator, but it proceeded faster in the presence of one. The sonochemical reaction was inhibited by hydroquinone.

While the immersion-type ultrasound generator is a highly effective source of ultrasound, a synthetically useful level of acceleration may be obtained also with an ultrasound cleaning bath. Thus, in a cleaning bath at ca. 20 °C, the hydrostannation of 1-hexyne (5 equiv) with Ph_3SnH (a 0.5 M toluene solution) produced the vinylstannane in 83% yield, while the same reaction without irradiation at 20 °C proceeded in 21% yield. This experiment also indicates that the sonochemical acceleration is not caused by a metallic contaminant which might enter the reaction mixture from the titanium horn immersed into the sonicated solution.

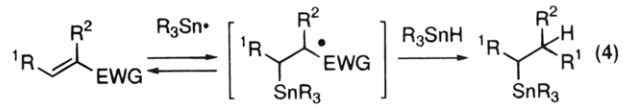
Interestingly, the sonochemical reaction in THF proceeded more rapidly than in toluene. Thus, sonochemical hydrostannation of phenylacetylene with Ph_3SnH proceeded at −55 °C (internal temperature) to afford the desired product in 61% yield (87% cis, Table 1, entry 7), while in toluene (entry 6) it took more than 13 h to achieve comparable conversion (see also entries 2 and 3). Since no large solvent effects were observed in control experiments without ultrasound and the rate of radical chain reaction is generally insensitive to reaction medium, it can be speculated that thermolysis of THF in an acoustic cavity may have generated a chain-initiating radical species.

In Table 1 are summarized examples of hydroxystannation reaction under ultrasound irradiation. Electron-withdrawing substituents facilitate the addition of the tin radicals to olefins, as illustrated by the smooth reaction of acrylic acid derivatives (eq 4, entries 10−12). Comparison of the sonochemical reactions (Table 1, columns 4−6) and the control experiments at the same low temperature (columns 8 and 9) indicated that the rate

Scheme 1



acceleration[17] by ultrasound irradiation may be on the order of >100.



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In light of the physics of ultrasound irradiation, we can account for the foregoing observations by a hypothesis (Scheme 1) that an initiating radical species formed in the hot cavity[18] diffuses into a cold bulk medium after adiabatic collapse of the cavity, and the product-forming propagation reaction continues there. Several lines of evidence supported this hypothesis. First, the high degree of kinetic cis selectivity of the hydrostannation strongly supports the notion that the vinylstannanes are formed in the low-temperature medium rather than in the hot cavity. Second, we found that the overall reaction rate is sensitive to the temperature of the bulk medium. Thus, the hydrostannation reaction of 1-hexyne with Ph_3SnH in toluene slowed down significantly as the temperature was lowered from 7 to −15 to −30 °C (Figure 2). If the product were formed in the hot cavity, such a small temperature change would not have an effect on the reaction rate. In addition, high temperature raises the vapor pressure of a solvent and makes acoustic cavitation less effective and hence should slow down the reaction.[19] Finally, the kinetic cis stereoselectivity that improves at lower bulk temperatures (Table 1, entries 4, 5, and 7) also indicates that the product forms in the bulk medium.[20]

We next compared the sonochemical radical initiation with two other common methods of radical initiation, photochemical (100-W high-pressure mercury lamp with Pyrex filter) and chemical (10 mol % Bu_3B),[21] for the reaction of Ph_3SnH with excess 1-hexyne (5 equiv). For

(17) The reaction rate did not fit into simple kinetic expression, but we could evaluate approximate rate acceleration as 100−600 by assuming first-order kinetics under the conditions of using excess olefin.

(18) The nature of this species is not clear: the initiation step may be either direct or molecular oxygen initiated homolysis of the Sn−H bond or thermolytic decomposition of solvent (e.g., THF).

(19) Suslick, K. S.; Gawienowski, J. J. Schubert, P. F.; Wang, H. H. *Ultrasonics* **1984**, *22*, 33.

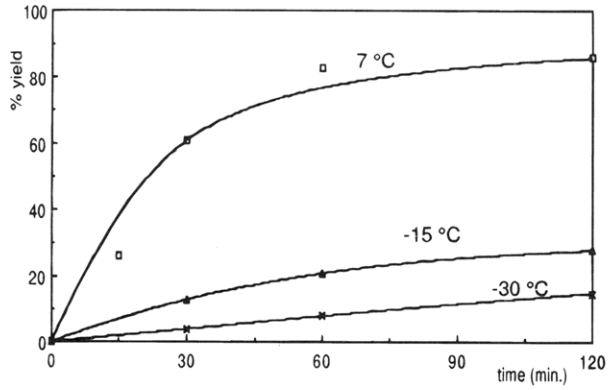


Figure 2. Effect of the variation of the bulk medium temperature on the reaction rate of the hydrostannation reaction. A mixture of 1-hexyne (5 equiv) with Ph_3SnH in 0.25 M toluene with 10 mol % AIBN was irradiated at three different temperatures.

Table 2. Comparison of Sonochemical, Photochemical, and Chemical Initiation[a]

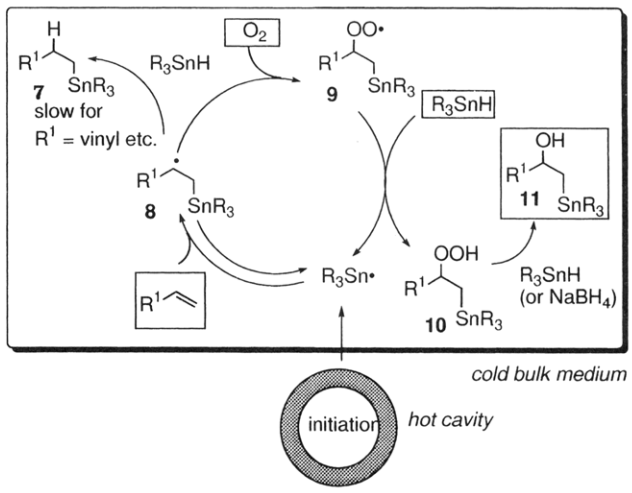
solvent	time (min)[b]	sono	photo	Bu_3B
toluene	60	83 (85)	97 (81)	90 (86)
Et_2O	15	53 (91)	98 (79)	100 (84)
THF	15	72 (93)	100 (49)	100 (89)
diglyme	15	78 (91)	89 (41)	100 (88)

[a] All reactions were performed under argon in a 0.25 M solution in an ice bath. The temperature of the bulk solvent was 7 °C in the sonochemical reaction. The photochemical reaction was carried out with a 100-W high-pressure mercury lamp with a Pyrex filter. [b] Final yield of the reactions were >90%, and hence the yields may be viewed as a semiquantitative measure of reaction rate in each solvent.

the purpose of comparison, the reactions were terminated at a short reaction period. Comparison of the "efficiency" of these methods may be meaningless due to the vastly different nature of the methods. However, the results in Table 2 suggest that the sonochemical method may be effective in generating less chain-carrying tin radical species. In a separate control experiment, the photoactivation was found to effect rapid cis/trans isomerization of the product. Under ultrasound irradiation, the vinylstannane product was found to be stereochemically stable.

Hydroxystannation of Olefins. The above observations demonstrated that homogeneous sonochemistry provides an opportunity to carry out a radical chain reaction with different initiation and propagation temperatures. In the above studies, we took advantage of this unique chemistry only to control stereochemistry. In the following studies, we explored it for the development of a new reaction.

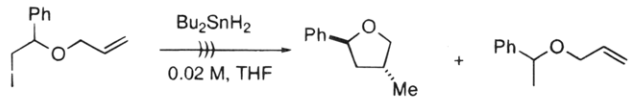
Scheme 2



In the hydrostannation reaction, the intermediate carbon radicals **4** (eq 3) and **6** (eq 4) abstract hydrogen from the tin hydride. During the course of the investigations, it occurred to us that one can trap these intermediates with molecular oxygen to achieve double functionalization of C−C multiple bond (eq 1). For this "hydroxystannation" reaction, one can draw the radical chain mechanism shown in Scheme 2. Realization of such a reaction appeared, by no means, to be easy. The reaction of $R_3Sn^•$ with molecular oxygen is an extremely fast reaction with a rate constant of $>10^9\ M^{-1}\ s^{-1}$ for $Bu_3Sn^•$,[22] while the addition of this tin radical to methyl methacrylate is 60 times slower.[23] However, there is a good chance that the latter reaction can effectively compete with the former, since the solubility of oxygen is very low in an organic solvent (8.3×10^{-3} M at 20 °C)[24] and the olefin concentration can be made as high as 0.1−1 M, on the other hand. We found that it is indeed the case; namely, sonochemical hydroxystannation of an olefin can be achieved by oxygen trapping of the radical **8**, when the olefin is activated by conjugation with an electron-withdrawing group. Formation of the hydrostannation product **7** was almost completely suppressed by the predominance of the oxygen-trapping pathway. However, the vinyl radical **4** formed in the reaction of an acetylene (eq 3) reacted faster with the tin hydride reagent than with oxygen and therefore failed to give hydroxystannation products.

Details of the hydroxystannation of an olefin with a tin hydride reagent in the presence of molecular oxygen were investigated for the reaction of 1-phenylbutadiene with Ph_3SnH (3 equiv) in toluene (eq 5). *Hydro*stannation of the diene is a slow reaction at low temperature. Thus, under argon or nitrogen, a mixture of the diene, Ph_3SnH (3 equiv), and a small amount of AIBN did not react to any appreciable extent at ca. 10 °C (note: *no reaction took place even under sonication*). Aeration did not cause any appreciable consumption of starting materials, either. However, when the aerated solution was

(20) There was found a similar temperature dependence of the stereochemistry of a radical cyclization reported in ref 2. Thus, the cyclization stereochemistry in the reaction below improved as the bulk temperature was lowered. The increased bimolecular competition (i.e., simple reduction) also reflects the temperature effects.



	% yield (trans:cis)	
70 °C, 0.2 h (w/o ultrasound)	99% (79:21)	1%
6 °C, 2 h	96% (87:13)	4%
-55 °C, 13 h	69% (94:6)	9%

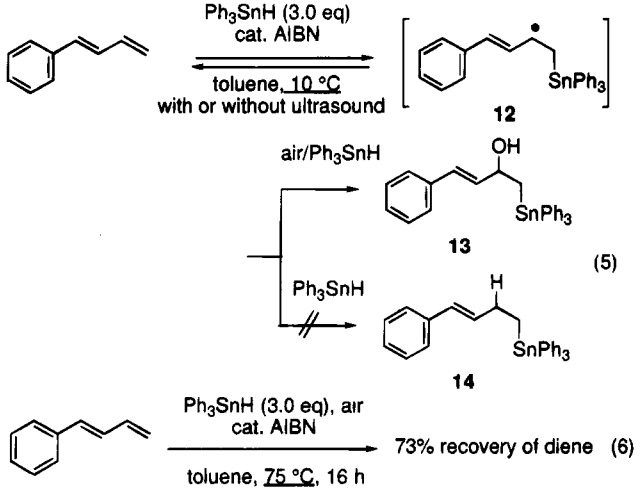
(21) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1987**, *28*, 3709.

(22) Mailland, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

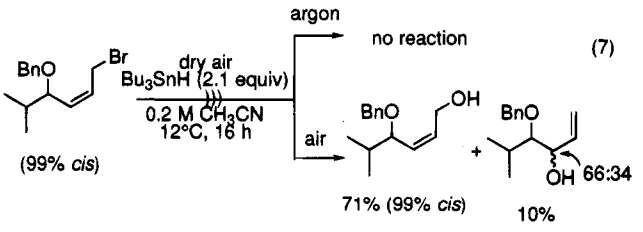
(23) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

(24) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163.

irradiated with ultrasound at 10 °C, smooth *hydroxy*stannation took place and produced the β-hydroxy stannane **13** (eq 5) in 71% isolated yield. Simple *Hydro*stannation products such as **14** were not produced at all. When the same reaction was carried out at a higher temperature (75 °C), oxidative loss of the tin hydride reagent took place and the starting diene was recovered (73%, eq 6). The high-temperature reaction without irradiation also resulted in the simple loss of the tin hydride, indicating that the temperature is as important as the ultrasound (cavitation and mixing). When pure oxygen gas was used instead of air, oxidative loss of the tin hydride predominated over the hydroxystannation, indicating that the low partial pressure of oxygen in air is just suitable for this subtly balanced reaction.

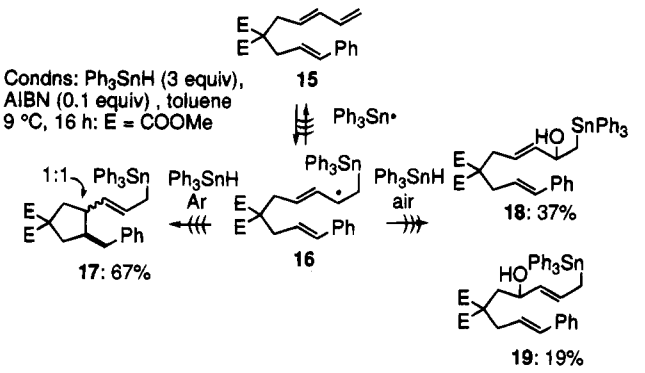


The above experiments can be rationalized by assuming reversible generation of allylic radical **12** (or **8** in Scheme 2), which is reactive only to oxygen and not to Ph_3SnH at low temperature. This was supported by the following experiments. First, at low temperature, an allylic bromide is not reduced by a tin hydride reagent but is only oxidized by molecular oxygen (eq 7).[4] Thus, irradiation of a mixture of an allylic bromide and Bu_3SnH at 10 °C under argon results in the recovery of the starting materials; yet, upon aeration, the irradiated solution starts smooth conversion of the bromide to oxygenated products.



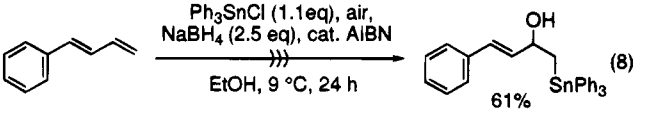
Although the lack of reaction between a tin hydride and a diene at low temperature *under argon* (eq 5) may also be taken as an indication of lack of interactions between two reactants, an intramolecular trapping probe (Scheme 3) provided evidence that this is not the case. Thus, sonication of a mixture of a triene (**15**) and Ph_3SnH (3 equiv) at 9 °C *under argon* smoothly produced the cyclization product **17** in 67% yield,[25] which indicates

Scheme 3



that the allylic radical **16** does form under the sonochemical conditions.[26] When the same irradiated mixture was aerated, the *hydroxy*stannation products **18** and **19** formed in 56% combined yield with 10% recovery of **15** with little trace of **17**. Thus, intermolecular trapping with molecular oxygen is much faster than intramolecular cyclization.

The foregoing observations indicate that molecular oxygen drives the chain reaction (Scheme 2) by selectively trapping the allylic radical **8** (R^1 = vinyl) to form the peroxy radical **9** and eventually the alcohol **11**. More than 2 equiv of the tin hydride reagent is necessary for this reaction, since 1 equiv is consumed for the conversion of the hydroperoxide **10** to the alcohol **11**. This is obviously inconvenient from a synthetic viewpoint. We found that this problem can be circumvented with $NaBH_4$, which allows the use of only 1 equiv of more experimentally convenient Ph_3SnCl as the tin source (eq 8). Thus, the tin chloride is reduced in situ with $NaBH_4$ to the tin hydride and the second equivalent of $NaBH_4$ rapidly reduces the hydroperoxide intermediate **10** to afford the stannyl alcohol **11**. Typically, a nearly stoichiometric mixture of a diene and Ph_3SnCl in ethanol was aerated first, sonication started, $NaBH_4$ added, and sonication continued for several hours in a ice-cold bath to obtain the product in a yield slightly lower than that by the stoichiometric procedure.

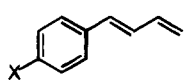
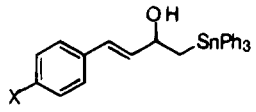
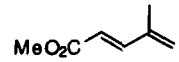
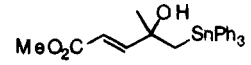
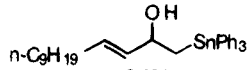
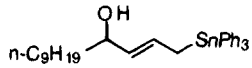
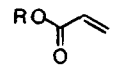
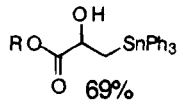
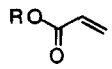
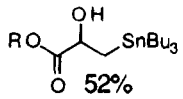
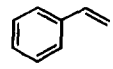
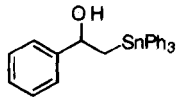


Representative results of hydroxystannation are shown in Table 3. To our pleasant surprise, the hydroxystannanes are quite stable: they can be readily purified by silica gel chromatography and made analytically pure. Dienes were found to be a particularly good substrate for the reaction (entries 1–6). Initial addition of a tin radical selectively takes place at the terminal position of the olefinic substrate. Internal dienes failed to be the substrates of this reaction. For the structural variation of *p*-substituted phenylbutadienes (entries 1–4), an electron-donating group was found to reduce the yield, in consonance with the nucleophilic character of a tin radical. In entry 2, the tin hydride was oxidized faster than consumption of the diene, which was recovered. For the hydroxystannation of 1,3-dienes further conjugated to a π-acceptor at the 4-position, 1,2-hydroxystannation

(25) The generality of this hydrostannation cyclization reaction was recently established: Hanessian, S.; Léger, R. *J. Am. Chem. Soc.* **1992**, *114*, 3115.

(26) Attempts to trap the benzylic radical intermediate prior to the formation of **17** by increasing oxygen concentration resulted in the formation of **18** and **19** due to direct trapping of **16**.

Table 3. Sonochemical Hydroxystannation[a]

entry	olefin	method	product (%)
			
1	X = H	A	71%
		B	71%
2[b]	X = MeO	A	25%
3	X = Cl	A	73%
		B	62%
4	X = MeO_2C	A	81%
		B	67%
5			
		A	80%
		B	44%
6[c]	n-C_9H_{19} 	A	 24%
			 29%
7[d]	 R = 2-ethylhexyl	A	 69%
8[e]	 R = 2-ethylhexyl	A	 52%
9[f]			
		A	70%
		B	62%

[a] The reactions were carried out in a 0.25 M toluene solution at 7–10 °C. Yields are based on pure isolated material (except in entry 7, NMR analysis with an internal standard). Method A: stoichiometric procedure with 3.0 equiv of Ph_3SnH and 0.1 equiv of AIBN. Method B: $Ph_3SnCl/NaBH_4$ procedure with 1.1 equiv of Ph_3SnCl, 2.5 equiv of $NaBH_4$, and 0.1 equiv of AIBN. [b] Ca. 30% of diene was recovered. [c] Ca. 20% of diene was recovered. [d] Ph_3SnH was added over 10 h. Hydrostannation product was formed in 4% yield, and 15% of the ester was recovered. [e] Bu_3SnH was used. Hydrostannation product formed in 25% yield. [f] Ph_3SnH was added over 10 h.

always takes place to produce a resonance-stabilized olefinic product (entries 1–5). However, a mixture of 1,2- and 1,4-hydroxystannation may result for electronically unbiased substrates (entry 6). This may be due to 1,3-isomerization of the allylic peroxy radical **9**.[27] In the line with such analysis, if the diene bears a suitable C-2 substituent (**20**), the hydroxystannation takes place exclusively in a 1,4-fashion, as shown in eq 9. The product **22** was predominantly (~3:1) trans. This stereochemistry probably reflects the geometry of the intermediate **21**, since allylic radicals do not isomerize under the present conditions.[4] The 1,4-hydroxystannation is thus useful for the synthesis of a new class of allylic stannanes.

(27) Cf. Porter, N. A.; Kaplan, J. K.; Dussault, P. H. *J. Am. Chem. Soc.* **1990**, *112*, 1266.

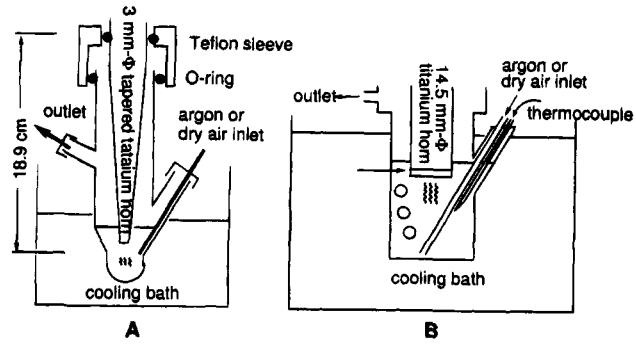
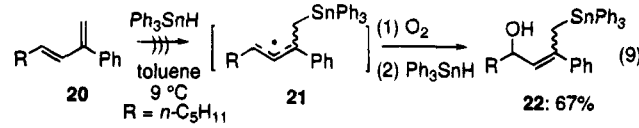


Figure 3. Sonochemical reactors based on the one described by Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73.



Hydroxystannation of olefins conjugated with a carbonyl or an aryl group also takes place smoothly. Thus, the reaction of an alkyl acrylate took place in good yield (entries 7 and 8). As seen from these examples, both Ph_3SnH and Bu_3SnH can be used for the hydroxystannation, while the latter gave lower yield due to formation of a hydrostannation product. The hydroxystannation of styrene gave a 1-phenyl-2-stannylethanol in 70% yield (entry 9). The reaction of nonconjugated olefins cannot effectively compete with the oxidative loss of the tin radical. Thus, attempted hydroxystannation of norbornene gave back the starting olefin. An attempted reaction with a 3,3-dialkoxy-1-cyclopropene resulted in hydrostannation.

In summary, we have shown that radical reactions initiated in the hot acoustic cavity undergo chain propagation involving a tin radical as a chain carrier. Since the bulk temperature may be varied simply by changing the temperature of the cooling bath, and the cavity temperature can be controlled by suitable choice of the medium (i.e., its vapor pressure), we can control, in principle, the initiation and the propagation temperatures independently to achieve selectivity previously unavailable for the radical reactions. Among other methods for radical initiation such as thermal, photochemical, and chemical ones, the sonochemical initiation appears to be the least effective in term of the number of radicals generated in the hot cavity. On the other hand, the sonochemical method can be more selective than others.

Experimental Section

General. Sonochemical experiments were carried out in the apparatus shown in Figure 3 with an immersion-type ultrasound generator (TOMY Co., Tokyo, 200 W, 20 KHz, wavelength 25.6 cm). The sonochemical reactions in this paper were carried out in the reactors shown in Figure 3. The reactor **A** is for small scale experiments (ca. 3 mL of solution) with a titanium horn of 3-mm diameter. Reactor **B** is for larger scale experiments (ca. 20 mL of solution) with a horn of 14.5-mm diameter. The rate of the sonochemical reactions was found to be rather insensitive to the irradiation power,

and 10–20% of the full power was enough to obtain a maximum rate. Qualitatively speaking, the use of more power only resulted in excessive heat formation. Note that the bottom flat surface of the titanium horn deteriorates (loss of flatness) after many runs and thus the efficiency of sonication suffers significantly. Routine chromatography was carried out as described by Still.[28] ^{1}H NMR (200, 270, and 500 MHz) and ^{13}C NMR (50, 67.5, and 125 MHz) spectra were measured for a $CDCl_3$ or CD_3CN solution of a sample on JEOL FX-200, GSX-270, and GSX-500 instruments, respectively. ^{1}H NMR spectra are reported in parts per million from internal tetramethylsilane, and ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO IR-800; absorptions are reported in cm^{-1}.

Hydrostannation of Phenylacetylene. A solution of Ph_3SnH (2.59 mL, 10.0 mmol) in toluene (4.1 mL) in the apparatus **B** was cooled in an ice bath under nitrogen. To this solution was added phenylacetylene (3.32 mL, 30.0 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 10 °C at a 25% power level of a 200-W machine). The reaction was over after 25 min (NMR), and after 1 h, the reaction mixture was filtered through a pad of Hyflo-Super-Cel and the filtrate was concentrated in vacuo. Purification on silica gel (0–10% AcOEt in hexane) gave 3.44 g (76%).

Other reactions in Table 1 were carried out in a similar manner. All hydrostannation products in this article are known compounds.

Hydrostannation Experiments for Mechanistic Studies. Ph_3SnH (64 μL, 0.25 mmol), triphenylbenzene (an internal standard, 20 mg), and AIBN (4.0 mg, 0.025 mmol) were dissolved in degassed toluene in apparatus **A**. 1-Hexyne (0.14 mL, 1.25 mmol) was added, and the reaction vessel was purged with argon. With cooling at a suitable outer temperature, the mixture was irradiated with ultrasound, while the internal temperature was monitored. Sample aliquots were withdrawn with a syringe, and excess hydroquinone was added before quantitative GLC analysis of the mixture.

The photochemical reaction was carried out in a similar manner but with a 100-W high-pressure mercury lamp with a Pyrex filter shone at a 10 cm-distance.

Hydrostannation Reaction by the Stoichiometric Procedure (Method A): (*E*)-4-Phenyl-1-(triphenylstannyl)but-3-en-2-ol. Into a toluene solution (1.62 mL) of AIBN (8.2 mg, 0.050 mmol) and 1-phenyl-1,3-butadiene (71 μL, 0.50 mmol) in apparatus **A** was bubbled dry air through a 0.8-mm i.d. Teflon tube at a rate of 10 mL/min. This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 10% EtOAc in hexane) to obtain 164.8 mg (71%) of the title compound: IR (CCl_4, cm^{-1}) 3450, 3050, 1955, 1880, 1820, 1480, 1425, 1075, 965, 905, 730, 695, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 1.85 (d, J = 3.7 Hz, 1 H), 1.96 (d, J = 7.1 Hz, 2 H), 4.71 (ddt, J = 3.7, 6.6, 7.1 Hz, 1 H), 6.25 (dd, J = 6.6, 15.9 Hz, 1 H), 6.39 (d, J = 15.9 Hz, 1 H), 7.16–7.61 (m, 20 H). Anal. Calcd for $C_{28}H_{26}OSn$: C, 67.64; H, 5.27. Found: C, 67.76; H, 5.47.

Slow addition of the tin hydride slightly improved the yield for relatively unreactive olefins.

Hydrostannation by the Tin Chloride/$NaBH_4$ Procedure (Method B): (*E*)-4-Phenyl-1-(triphenylstannyl)but-3-en-2-ol. Into an ethanol solution (2.0 mL) of Ph_3SnCl (212.0 mg, 0.55 mmol), $NaBH_4$ (46.7 mg, 1.25 mmol), AIBN (8.2 mg, 0.05 mmol), and 1-phenyl-1,3-butadiene (71 μL, 0.50 mmol) in apparatus **A** was bubbled dry air through a 0.8-mm i.d. Teflon tube at rate of 10 mL/min. This solution was cooled in an ice bath and irradiated with ultrasound (internal temperature 9 °C). After 24 h, the reaction mixture was filtered through Hyflo-Super-Cel. The filtrate was concentrated under reduced pressure and purified on silica gel (eluent 10% EtOAc in hexane) to obtain 149.2 mg (60%) of the the title compound.

On a larger scale run in apparatus **B**, air was bubbled (via a 1-mm i.d. Teflon tube; ice bath, internal temperature of 7–10 °C) into a mixture of the diene (0.50 g, 3.84 mmol), Ph_3SnCl (1.63 g, 4.22 mmol), and AIBN (0.06 g, 0.38 mmol) in 10 mL of ethanol, which was sonicated. $NaBH_4$ (0.431 g, 11.5 mmol) was added, and bubbling was continued for 9 h. Ethanolamine (1.6 mL) was added. Aqueous extractive workup afforded 1.67 g of the crude product, from which 1.36 g (71%) of the product was isolated by silica gel chromatography.

(*E*)-4-(4-(Methoxycarbonyl)phenyl-1-(triphenylstannyl)-but-3-en-2-ol. Method A. Into a toluene solution (1.62 mL) of AIBN (8.2 mg, 0.050 mmol) and (*E*)-1-(4-(methoxycarbonyl)-phenyl)-1,3-butadiene (93.6 mg, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 20% EtOAc in hexane) to obtain 225.4 mg (81%) of the title compound: IR (CCl_4, cm^{-1}) 3600, 3060, 1950, 1860, 1820, 1725, 1610, 1430, 1280, 1110, 725, 700, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 1.89 (d, J = 3.9 Hz, 1 H), 1.97 (d, J = 7.1 Hz, 2 H), 4.75 (ddt, J = 3.9, 5.6, 7.1 Hz, 1 H), 6.35 (dd, J = 5.6, 15.9 Hz, 1 H), 6.42 (d, J = 15.9 Hz, 1 H), 7.20 (d, J = 8.3 Hz, 2 H), 7.26–7.78 (m, 15 H), 7.92 (d, J = 8.3 Hz, 2 H).

Anal. Calcd for $C_{30}H_{28}O_3Sn$: C, 64.90; H, 5.08. Found: C, 65.15; H, 5.19.

Method B. Into an ethanol (2.0 mL) solution of Ph_3SnCl (212.0 mg, 0.55 mmol), $NaBH_4$ (46.7 mg, 1.25 mmol), AIBN (8.2 mg, 0.050 mmol), and (*E*)-1-(4-(methoxycarbonyl)phenyl)-1,3-butadiene (93.6 mg, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath and irradiated with ultrasound (internal temperature 9 °C). After 24 h, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified on silica gel (eluent 20% EtOAc in hexane) to obtain 185.8 mg (67%) of the title compound.

(*E*)-4-(4-Chlorophenyl)-1-(triphenylstannyl)but-3-en-2-ol. Method A. Into a toluene solution (1.55 mL) of AIBN (8.2 mg, 0.050 mmol) and (*E*)-1-(4-chlorophenyl)-1,3-butadiene (76 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 13% EtOAc in hexane) to obtain 193.9 mg (73%) of the title compound: IR (CCl_4, cm^{-1}) 3380, 3000, 1955, 1895, 1820, 1730, 1490, 1425, 1070, 910, 725, 700, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 1.87 (d, J = 3.9 Hz, 1 H), 1.96 (d, J = 7.1 Hz, 2 H), 4.70 (ddt, J = 3.9, 6.5, 7.1 Hz, 1 H), 6.21 (dd, J = 6.5, 15.9 Hz, 1 H), 6.33 (d, J = 15.9 Hz, 1 H), 7.05–7.70 (m, 19 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) 23.57, 71.50, 127.62 (2 C), 128.10, 128.26 (2 C), 128.51 (6 C), 128.86 (3 C), 133.15, 134.71, 134.94, 136.78, 137.05 (6 C), 138.16 (3 C).

Anal. Calcd for $C_{28}H_{25}OClSn$: C, 63.26; H, 4.74. Found: C, 63.30; H, 4.50.

Method B. Into an ethanol (2.0 mL) solution of Ph_3SnCl (212.0 mg, 0.55 mmol), $NaBH_4$ (46.7 mg, 1.25 mmol), AIBN (8.2 mg, 0.050 mmol), and (*E*)-1-(4-chlorophenyl)-1,3-butadiene (76 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath and irradiated with ultrasound (internal temperature (9 °C). After 24 h, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified on silica gel (eluent 13% EtOAc in hexane) to obtain 164.8 mg (62%) of the title compound.

(*E*)-4-(4-Methoxyphenyl)-1-(triphenylstannyl)but-3-en-2-ol. Into a toluene solution (1.55 mL) of AIBN (8.2 mg, 0.050 mmol) and (*E*)-1-(4-methoxyphenyl)-1,3-butadiene (80.1 mg, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 30% EtOAc in hexane) to obtain 66.7 mg (25%) of the title compound: IR (CCl_4, cm^{-1}) 3610, 3060, 2990, 1945, 1880, 1820, 1515, 1430, 1250, 1175, 1040,

(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

725, 700; ^{1}H NMR (200 MHz, $CDCl_3$) 1.88 (d, J = 3.4 Hz, 1 H), 1.96 (d, J = 7.8 Hz, 2 H), 3.79 (s, 3 H), 4.71–4.82 (m, 1 H), 6.14 (dd, J = 7.6, 16.2 Hz, 1 H), 6.30 (d, J = 16.2 Hz, 1 H), 6.83 (d, J = 8.6 Hz, 2 H), 7.21 (d, J = 8.6 Hz, 2 H), 7.33–7.61 (m, 15 H).

Methyl 4-Hydroxy-4-methyl-5-(triphenylstannyl)-2-pentenoate. Method A. Into a toluene solution (1.62 mL) of AIBN (8.2 mg, 0.050 mmol) and methyl 4-methyl-2,4-pentadienoate (67 μL, 0.50 mmol) was bubbled dry air (10 mL/min) at 0 °C. Ph_3SnH (0.38 mL, 1.5 mmol) was added, and the reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 30% EtOAc in hexane) to obtain 199.2 mg (80%) of the title compound: IR (neat, cm^{-1}) 3450, 3075, 1960, 1890, 1820, 1705, 1435, 1310, 1285, 1075, 735, 700, 450; ^{1}H NMR (200 MHz, $CDCl_3$) 1.40 (s, 3 H), 1.72 (s, 1 H), 1.99 (s, 2 H), 3.67 (s, 3 H), 5.87 (d, J = 15.6 Hz, 1 H), 7.02 (d, J = 15.6 Hz, 1 H), 7.22–7.69 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) 28.48, 31.05, 51.51, 73.41, 117.08, 128.50 (6 C), 128.86 (3 C), 137.09 (6 C), 138.22 (3 C), 155.20, 176.44.

Anal. Calcd for $C_{25}H_{26}O_3Sn$: C, 64.90; H, 5.08. Found: C, 65.15; H, 5.19.

Method B. Into an ethanol solution (2.0 mL) of Ph_3SnCl (212.0 mg, 0.55 mmol), $NaBH_4$ (46.7 mg, 1.25 mmol), AIBN (8.2 mg, 0.050 mmol), and methyl 4-methyl-2,4-pentadienoate (67 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath and irradiated with ultrasound (internal temperature 9 °C). After 24 h, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified on silica gel (eluent 30% EtOAc in hexane) to obtain 109.6 mg (44%) of the title compound.

(*E*)-2-Hydroxy-1-(triphenylstannyl)-3-dodecene and (*E*)-4-Hydroxy-1-(triphenylstannyl)-2-dodecene. Into a toluene solution (1.51 mL) of AIBN (8.2 mg, 0.050 mmol) and 1,3-dodecadiene (117 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 10–30% EtOAc in hexane) to obtain 79.9 mg (29%) of (*E*)-2-hydroxy-1-(triphenylstannyl)-3-dodecene and 66.5 mg (24%) of its regioisomer, (*E*)-4-hydroxy-1-(triphenylstannyl)-2-dodecene.

(E)-2-Hydroxy-1-(triphenylstannyl)-3-dodecene: IR (neat, cm^{-1}) 3400, 2950, 1955, 1880, 1820, 1575, 1480, 1425, 1070, 695, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 0.89 (t, J = 6.9 Hz, 3 H), 1.15–1.36 (br s, 14 H), 1.65 (d, J = 3.4 Hz, 1 H), 1.82–1.92 (br d, J = 7.0 Hz, 4 H), 4.42–4.45 (m, 1 H), 5.45–5.55, (m, 2 H), 7.30–7.72 (m, 15 H).

(E)-4-Hydroxy-1-(triphenylstannyl)-2-dodecene: IR (neat, cm^{-1}) 3350, 2850, 2750, 1955, 1880, 1815, 1655, 1580, 1430, 1070, 725, 700, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 0.88 (t, J = 7.1 Hz, 3 H), 1.08 (d, J = 3.2 Hz, 1 H), 1.10–1.50 (br s, 16 H), 2.41 (dd, J = 1.0, 8.4 Hz, 2 H), 3.83–3.96 (m, 1 H), 5.37 (ddt, J = 1.0, 7.4, 14.8 Hz, 1 H), 5.86 (ddt, J = 0.8, 8.4, 14.8 Hz, 1 H), 7.38–7.75 (m, 15 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) 14.03, 15.90, 22.67, 25.45, 29.14, 29.31, 29.46, 29.56, 31.88, 37.15, 73.32, 128.60 (6 C), 129.04 (3 C), 129.65, 131.31, 137.13 (6 C), 137.79 (3 C).

Anal. Calcd for $C_{31}H_{40}OSn$: C, 68.02; H, 7.73. Found: C, 68.23; H, 7.48.

2-Ethylhexyl 2-Hydroxy-3-(triphenylstannyl)propanoate. Method A. Into a toluene solution (1.23 mL) of AIBN (8.2 mg, 0.050 mmol) and 2-ethylhexyl acrylate (104 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C), and to the reaction mixture was added a toluene solution (1.00 mL) of Ph_3SnH 0.38 mL, 1.5 mmol) over 10 h with a syringe pump. After 24 h, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude reaction mixture was analyzed by quantitative ^{1}H NMR (CH_2Br_2 as an internal standard) to determine the yield of hydroxy stannane (69%) and purified on silica gel (eluent 10% EtOAc in hexane): IR (CCl_4, cm^{-1}) 3530, 2960, 1950, 1880, 1820, 1730, 1425, 1215, 1075, 910, 730, 700, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 0.81 (t, J = 3.0, 7.3 Hz, 3 H), 0.85 (t, J = 3.0, 7.3 Hz, 3 H), 1.25–1.50 (m, 9 H), 1.92 (dd, J = 9.5, 12.9 Hz, 1 H), 2.02 (dd, J = 5.4, 12.9 Hz, 1 H), 3.10 (d, J = 5.4 Hz, 1 H), 3.91 (ddd, J = 0.9, 6.1, 10.8 Hz, 1 H), 3.95 (ddd, J = 2.1, 6.1, 10.8 Hz, 1 H), 4.49 (ddd, J = 5.4, 5.4, 9.5 Hz, 1 H), 7.21–7.62 (m, 15 H).

Anal. Calcd for $C_{29}H_{36}O_3Sn$: C, 63.18; H, 6.58. Found: C, 63.42; H, 6.55.

(1-Hydroxy-2-(triphenylstannyl)ethyl)benzene. Method A. Into a toluene solution (1.00 mL) of AIBN (8.2 mg, 0.050 mmol) and styrene (57 μL, 0.50 mmol) was bubbled dry air (10 mL/min). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C), and to the reaction mixture was added a toluene solution (1.00 mL) of Ph_3SnH (0.64 mL, 2.5 mmol) over 10 h with a syringe pump. After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 10% EtOAc in hexane) to obtain 165.0 mg (70%) of the title compound: IR (neat, cm^{-1}) 3600, 3050, 1950, 1880, 1815, 1425, 1075, 1030, 725, 695, 445; ^{1}H NMR (200 MHz, $CDCl_3$) 2.05 (d, J = 3.7 Hz, 1 H), 2.09 (d, J = 8.1 Hz, 1 H), 5.07 (dt, J = 3.7, 8.1 Hz, 1 H), 7.19–7.67 (m, 20 H); ^{13}C NMR (125 MHz, $CDCl_3$) 24.43, 72.93, 125.33 (2 C), 127.50 (2 C), 128.19, 128.47 (6 C), 128.73 (3 C), 137.00 (6 C), 138.19 (3 C), 146.75.

Anal. Calcd for $C_{26}H_{24}OSn$: C, 66.28; H, 5.13. Found: C, 66.49; H, 4.89.

Method B. Into an ethanol solution (2.0 mL) of Ph_3SnCl (212.0 mg, 0.55 mmol), $NaBH_4$ (46.7 mg, 1.25 mmol), AIBN (8.2 mg, 0.050 mmol), and styrene (57 μL, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath and irradiated with ultrasound (internal temperature 9 °C). After 24 h, the reaction mixture was filtered, concentrated under reduced pressure, and purified on silica gel (eluent 10% EtOAc in hexane) to obtain 147.0 mg (62%) of the title compound.

Hydrostannation of 4,4-Bis(methoxycarbonyl)-1-phenyl-1,6,8-nonatriene (15). Into a toluene solution (1.60 mL) of AIBN (8.2 mg, 0.050 mmol) and 4,4-bis(methoxycarbonyl)-1-phenyl-1,6,8-nonatriene (157 mg, 0.50 mmol) was bubbled dry air (10 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.38 mL, 1.5 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 16 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 10–100% EtOAc in hexane) to obtain 57.9 mg (19%) of **18** and 126.2 mg (37%) of its regioisomer, **19**.

8-Hydroxy-4,4-bis(methoxycarbonyl)-1-phenyl-9-(triphenylstannyl)-1,6-nonadiene (18): IR (neat, cm^{-1}) 3450, 3040, 2830, 1940, 1870, 1810, 1720, 1420, 1250, 1190, 1065, 1010, 965, 900, 720, 685, 435; ^{1}H NMR (200 MHz, $CDCl_3$) 1.81 (d, J = 6.4 Hz, 2 H), 1.85 (d, J = 3.6 Hz, 1 H), 2.51 (d, J = 6.8 Hz, 2 H), 2.71 (d, J = 7.8 Hz, 2 H), 3.69 (s, 6 H), 4.47 (ddt, J = 3.6, 6.4, 7.6 Hz, 1 H), 5.41 (dt, J = 6.8, 15.1 Hz, 1 H), 5.63 (dd, J = 7.6, 15.1 Hz, 1 H), 5.96 (dt, J = 7.8, 15.9 Hz, 1 H), 6.40 (d, J = 15.9 Hz, 1 H), 7.20–7.69 (m, 20 H).

6-Hydroxy-4,4-bis(methoxycarbonyl)-1-phenyl-9-(triphenylstannyl)-1,7-nonadiene (19): IR (neat, cm^{-1}) 3400, 2950, 1950, 1880, 1820, 1730, 1430, 1260, 1190, 1065, 960, 900, 720, 685; ^{1}H NMR (200 MHz, $CDCl_3$) 1.24 (d, J = 6.4 Hz, 2 H), 1.61 (br s, 1 H), 2.66 (d, J = 6.4 Hz, 2 H), 2.78 (dd, J = 1.0, 7.1 Hz, 2 H), 3.73 (s, 3 H), 4.20–4.41 (m, 1 H), 5.48 (dt, J = 6.4, 15.6 Hz, 1 H), 5.62 (dd, J = 6.4, 15.6 Hz, 1 H), 6.01 (dt, J = 8.1, 15.9 Hz, 1 H), 6.43 (dt, J = 1.0, 15.9 Hz, 1 H), 7.21–7.70 (m, 20 H).

4-Hydroxy-2-phenyl-1-(triphenylstannyl)-2-nonene (22). Into a toluene solution (0.73 mL) of 2-phenyl-1,3-nonadiene (43.8 μL, 0.20 mmol) was bubbled dry air (2 mL/min). This solution was cooled in an ice bath, and to the solution was added Ph_3SnH (0.26 mL, 1.0 mmol). The reaction mixture was irradiated with ultrasound (internal temperature 9 °C). After 1 h, the reaction mixture was concentrated under reduced pressure and purified on silica gel (eluent 15% EtOAc in hexane) to obtain 79.4 mg (69%, *E*/*Z* ratio 2:1) of the title compound. The *E*/*Z* ratio was determined by ^{1}H NMR (olefinic

signals) of the crude product. The mixture was further purified by HPLC and characterized.

(*E*)-Isomer: IR (neat, cm^{-1}) 3400, 3060, 2930, 2850, 1955, 1880, 1815, 1630, 1430, 1075, 1020, 910, 760, 740, 695, 445; ^1H NMR (200 MHz, $CDCl_3$) 0.69 (d, J = 3.4 Hz, 1 H), 0.86 (t, J = 6.4 Hz, 3 H), 1.17–1.56 (m, 8 H), 2.83 (br s, 2 H), 4.20–4.34 (m, 1 H), 5.38 (d, J = 7.8 Hz, 1 H), 7.18–7.39 (m, 15 H).

(*Z*)-Isomer: IR (neat, cm^{-1}) 3380, 3050, 2930, 2850, 1955, 1880, 1815, 1635, 1425, 1075, 1020, 995, 910, 725, 695, 445; ^1H NMR (200 MHz, $CDCl_3$) 0.83 (t, J = 6.8 Hz, 3 H), 0.92 (d, J = 2.7 Hz, 1 H), 1.03–1.56 (m, 8 H), 2.76 (br s, 2 H), 3.98–3.93 (m, 1 H), 5.40 (d, J = 9.4 Hz, 1 H), 7.11–7.53 (m, 15 H).

Anal. Calcd for $C_{33}H_{36}OSn$: C, 69.86; H, 6.40. Found: C, 69.85; H, 6.27.

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