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Synthetic utility of tribenzyltin hydride and its derivatives as easily accessible, removable, and decomposable organotin reagents

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ABSTRACT

Radical reactions using tribenzyltin hydride (Bn_3SnH) easily prepared from tin and benzyl chloride were studied. The Et_3B-initiated reduction and cyclization of haloalkanes and haloalkenes with Bn_3SnH proceeded efficiently. Homolytic hydrostannylation of alkynes with Bn_3SnH followed by treatment with electrophiles gave functionalized alkenes in good to high yields. The organotin byproducts formed could be easily removable by filtration and silica-gel column chromatography without any pretreatment. It was also found that tribenzyltin chloride (Bn_3SnCl) easily decomposed to benzyl alcohol in a basic solution of H_2O_2.

1. Introduction

Triorganotin hydrides (R_3SnH) are highly valuable as radical mediators and stannylating agents [1–4]. Particularly, tributyltin hydride (Bu_3SnH) is commercially available and has frequently been used to these ends. Radical reactions mediated by R_3SnH provide chemo- and stereoselective methods not only for reduction of organic halides and pseudohalides but also for inter- and intramolecular C–C bond formation [5]. Hydrostannylation of alkynes and alkenes with R_3SnH is convenient to prepare alkenyl- and alkylstannanes [1–4,6], which are synthetically useful for further transformations utilizing the C–Sn bonds formed [2,4,7]. Unfortunately, synthetic use of Bu_3SnH and their derivatives has two serious problems. Since the organotin byproducts Bu_3SnX (X = halogen, OH, $OSnBu_3$) have high lipophilicity, their removal by silica-gel column chromatography is difficult without pretreatment of the reaction mixture [1,8]. In addition, Bu_3SnX are stable, hardly decomposable, and toxic [9]. Thus far a variety of R_3SnH have been developed to facilitate product isolation [1–3]. However, the preparation of these reagents is costly and laborious. We herein report synthetic utility of tribenzyltin hydride (Bn_3SnH) as an easily accessible, removable, and decomposable substitute for Bu_3SnH.

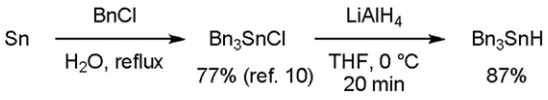
2. Results and discussion

2.1. Synthesis of Bn_3SnH

Bn_3SnH can be prepared from tin and benzyl chloride by two steps (Scheme 1). The first step is the aqueous reaction of tin with benzyl chloride [10]. The Bn_3SnCl obtained was rapidly and efficiently converted into Bn_3SnH by treatment with $LiAlH_4$ [11,12]. Bn_3SnH, a white solid, is storable in a sealed bottle purged with an inert gas at −20 °C (in a refrigerator). Under the atmosphere Bn_3SnH can be handled at room temperature in several minutes although it gradually decomposes. On exposure to air for 1 day at room temperature, Bn_3SnH suffered *ca.* 70% conversion into unidentified products.

2.2. Reactivities of Bn_3SnH and alkenyltribenzylstannanes

To test the utility of Bn_3SnH, radical reduction of organic halides was first conducted. In the presence of Et_3B as radical initiator, Bn_3SnH reacted smoothly with various simple and functionalized haloalkanes **1** at room temperature to give the corresponding dehalogenated products **2** in high yields (Table 1) [13]. Like Bu_3SnH,



Scheme 1. Synthesis of Bn_3SnH.

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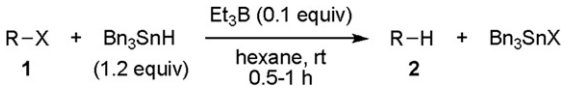
Table 1
Reduction of haloalkanes **1** with Bn_3SnH.[a]



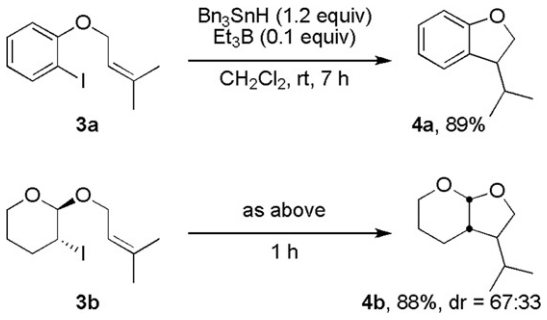
Entry	R–X	Product	Yield (%)[b]
1	n-$C_{12}H_{25}$–I (**1a**-I)	**2a**	96[c]
2	n-$C_{12}H_{25}$–Br (**1a**-Br)	**2a**	90[c]
3	$PhCO_2(CH_2)_4$-I (**1b**-I)	**2b**	96
4	$PhCO_2(CH_2)_4$-Br (**1b**-Br)	**2b**	97
5	$CH_3C(O)(CH_2)_{11}$–Br (**1c**)	**2c**	90
6	$CH_3CH(OH)(CH_2)_{11}$–Br (**1d**)	**2d**	92
7	$PhCH(OH)(CH_2)_5$–Br (**1e**)	**2e**	91
8	$CH_3CH(OTBS)(CH_2)_{11}$–Br (**1f**)	**2f**	95

[a] Unless otherwise noted, all reactions were carried out with **1** (0.50 mmol), Bn_3SnH (0.60 mmol) and Et_3B (1 M in hexane, 0.05 mL, 0.05 mmol) in hexane (2 mL).
[b] Isolated yield of **2**.
[c] Determined by GC analysis.

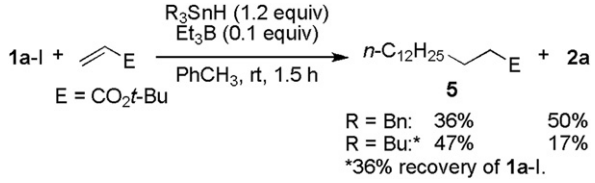
Bn_3SnH is reactive enough for radical reduction of haloalkanes. It is worthy of note that the tin byproducts Bn_3SnX (X = Br, I) precipitated in hexane and most of those could be removed by filtration. The crude product contaminated with a small amount of Bn_3SnX could be easily purified by silica-gel column chromatography without pretreatment. The methylene signals of the Bn_3Sn moiety completely disappeared in ^1H NMR spectra of the isolated products. Additionally Bn_3SnX do not have such an unpleasant smell as caused by Bu_3SnX. Thus Bn_3SnH turned out more convenient than Bu_3SnH from the viewpoint of product purification.

Bn_3SnH is useful also for radical cyclization. The Et_3B-initiated reactions of iodoalkenes **3a** and **3b** afforded the cyclized products **4a** and **4b**, respectively, in high yields (Scheme 2). The pure products were easily obtained by direct column chromatography of the concentrated reaction mixtures on silica-gel.

Bn_3SnH was next used for radical addition of 1-iododododecane (**1a**-I) to *t*-butyl acrylate (Scheme 3). In contrast to the successful radical cyclization, the Bn_3SnH-mediated intermolecular reaction resulted in a low yield of the desired adduct **5**. Since considerable formation of **2a** was observed, the discouraging result is

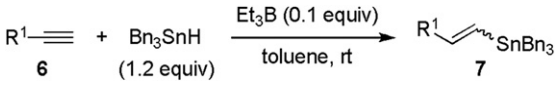


Scheme 2. Cyclization of haloalkenes **3** with Bn_3SnH.



Scheme 3. Intermolecular addition of 1-iododododecane with Bn_3SnH.

Table 2
Hydrostannylation of terminal alkynes with Bn_3SnH.[a]



Entry	R^1	Time (h)	Product	Yield (%)[b]	*E*:*Z*[c]
1	n-$C_{10}H_{21}$	3	**7a**	92	67:33
2	n-$C_{10}H_{21}$	12	**7a**	quant	81:19
3	$HO(CH_2)_4$	3	**7b**	82	64:36
4[d,e]	$HO(CH_2)_4$	24	**7b**	82	73:27
5[e]	c-C_6H_{11}	24	**7c**	85	78:22
6	Ph	3	**7d**	99	98:2
7	Me_3Si	24	**7e**	80	>99:1

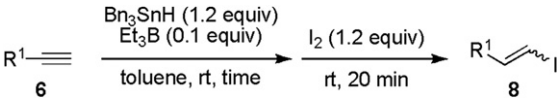
[a] Unless otherwise noted, all reactions were carried out with **6** (0.50 mmol), Bn_3SnH (0.60 mmol) and Et_3B (1 M in hexane, 0.05 mL, 0.05 mmol) in toluene (2 mL).
[b] Isolated yield of **7**.
[c] Determined by ^1H NMR analysis.
[d] With Bn_3SnH (0.70 mmol).
[e] With Et_3B (0.10 mmol).

attributable to fast hydrogen abstraction of the dodecyl radical intermediate from Bn_3SnH. Under the same conditions, the use of Bu_3SnH instead of Bn_3SnH improved the molar ratio of **5** to **2a** although the conversion of **1a**-I was not good. This fact implies that Bn_3SnH has higher hydrogen-donating ability than Bu_3SnH (*vide infra*).

In the presence of Et_3B, hydrostannylation of terminal alkynes **6** with Bn_3SnH proceeded efficiently with moderate to high *E*-selectivity (Table 2) [14,15]. Under the same conditions, the reaction of 1-dodecyne (**6a**) with Bu_3SnH gave the corresponding adduct in 5% yield (*E*:*Z* = 2:3, 92% recovery of **6a**). Thus Bn_3SnH is more reactive than Bu_3SnH toward homolytic hydrostannylation. The *E*-selectivity of alkenylstannanes **7** increased with the reaction time (entries 1–4). A most plausible explanation for this observation is that (*Z*)-**7** are isomerized to the thermodynamically favored *E*-isomers by addition and elimination (reversible addition) of a tribenzylstannyl radical ($Bn_3Sn^•$) [16].

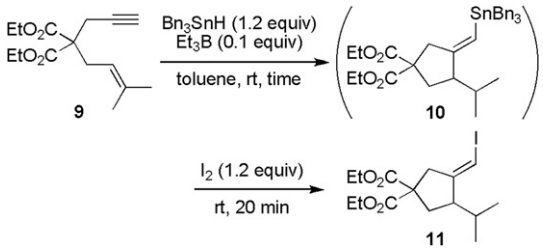
As shown in Table 2, the homolytic hydrostannylation of alkynes with Bn_3SnH provides a convenient route to alkenylstannanes bearing a tribenzylstannyl group. We therefore examined synthetic utility of these compounds by reaction with heteroatom and carbon electrophiles. Iodine was first employed as the electrophile. The Et_3B-initiated hydrostannylation followed by treatment with iodine in a one-pot manner gave iodoalkenes **8** in high yields without any problem of

Table 3
Hydrostannylation of terminal alkynes followed by iodonolysis.[a]



Entry	R^1	Time (h)	Product	Yield (%)[b]	*E*:*Z*[c]
1	n-$C_{10}H_{21}$	12	**8a**	88	80:20
2[d,e]	$HO(CH_2)_4$	24	**8b**	89	72:28
3[e]	c-C_6H_{11}	24	**8c**	81	82:18
4	Ph	3	**8d**	94	98:2

[a] Unless otherwise noted, all reactions were carried out with **6** (0.50 mmol), Bn_3SnH (0.60 mmol), Et_3B (1 M in hexane, 0.05 mL, 0.05 mmol), and iodine (0.60 mmol) in toluene (2 mL).
[b] Isolated yield of **8**.
[c] Determined by ^1H NMR analysis.
[d] With Bn_3SnH (0.70 mmol).
[e] With Et_3B (0.10 mmol).



Scheme 4. Cyclization of enyne **9** followed by iodonolysis.

purification (Table 3). These results clearly indicate that iodine reacts site-selectively at the alkenyl–Sn bond rather than at the benzyl–Sn bonds, and that alkenylstannanes **7** serve as efficient alkenyl donors. When enyne **9** was subjected to the same reaction conditions, cyclized iodoalkene **11** was formed as a single stereoisomer in 94% yield via radical cyclization of **9** to alkenylstannane **10** (Scheme 4) [17].

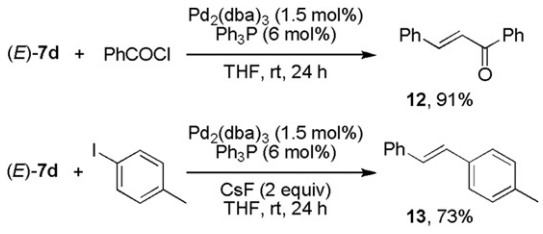
Alkenylstannanes **7** are valuable also for Pd-catalyzed cross-coupling reactions (Scheme 5) [7]. Under catalysis by $Pd_2(dba)_3$-PPh_3, (*E*)-**7d** reacted smoothly with benzoyl chloride. The crude product containing Bn_3SnCl could be directly purified by silica-gel column chromatography to give chalcone (**12**) in high yield. The cross-coupling between (*E*)-**7d** and *p*-iodotoluene proceeded in the presence of CsF. In these reactions, benzyl group transfer to the electrophiles was not observed.

2.3. Radical clock experiment

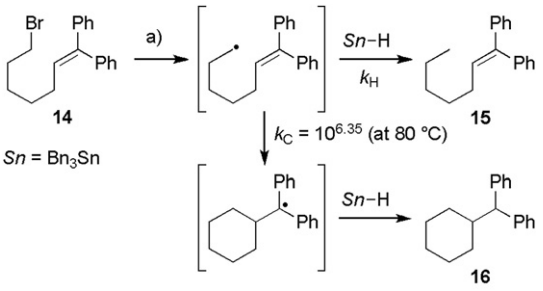
To evaluate the hydrogen-donating ability of Bn_3SnH, the rate constant for hydrogen abstraction by a primary alkyl radical (k_H (Bn_3SnH)) was determined by a radical clock experiment using bromoalkene **14** (Scheme 6) [18,19]. The reaction of **14** in the presence of a large excess of Bn_3SnH (pseudo-first-order conditions) gave acyclic product **15** and cyclic product **16** with the ratio of 1.73:1. This product ratio was used for the determination of k_H (Bn_3SnH) with the known rate constant for cyclization of the acyclic radical intermediate (k_C) and the average concentration of Bn_3SnH. The rate constant k_H (Bn_3SnH) was estimated to be 1.9×10^7, which is between the values of k_H (Bu_3SnH) (6.4×10^6) and k_H (Ph_3SnH) (2.2×10^7) [20]. This result proves that Bn_3SnH has higher hydrogen-donating ability than Bu_3SnH. The reactivity of Bn_3SnH well agrees with the fact that the Bn_3SnH-mediated addition of **1a**-I to *t*-butyl acrylate is subject to competitive reduction of **1a**-I to **2a** (Scheme 3). In addition, the fast hydrostannylation of alkynes with Bn_3SnH (Table 2) is probably because its high hydrogen-donating ability accelerates hydrogen abstraction of alkenyl radical intermediates formed by reversible addition of $Bn_3Sn^{\bullet}$ to alkynes.

2.4. Decomposability of Bn_3SnCl

Judging from the similarity of tributyltin compounds Bu_3SnX in LD_{50} (rat) values (X = Cl, 129 mg/kg; X = Br, 138 mg/kg; X = $OSnBu_3$, 87 mg/kg) [21], tribenzyltin compounds Bn_3SnX also have similar levels of acute toxicity, irrespective of the heteroatom substituent X. Since the LD_{50} (rat) value of Bn_3SnCl is reported to be 175 mg/kg [21], it is predicted that Bn_3SnX would be slightly more toxic than Bu_3SnX. However, as described above, tribenzyltin byproducts Bn_3SnX are easily removable. In addition, they are easily decomposable by treatment with a basic solution of H_2O_2. For example, the reaction of Bn_3SnCl with excess amounts of H_2O_2 and $KHCO_3$ in THF at 80 °C gave BnOH in 79% yield (Scheme 7) [22]. This yield corresponds to the cleavage of 2.4 carbon–tin bonds per one molecule of Bn_3SnCl. No methylene signals of the Bn_3Sn moiety were observed in ^1H NMR spectra of the crude product. The decomposition reaction proceeded even at room temperature.



Scheme 5. Pd-catalyzed cross-coupling reactions of alkenylstannane (*E*)-**7d**.



a) **14** (0.23 mmol), Bn_3SnH (2.46 mmol), AIBN (0.06 mmol), benzene (10 mL), 80 °C, 10 h.

Scheme 6. Radical clock experiment using bromoalkene **14**.

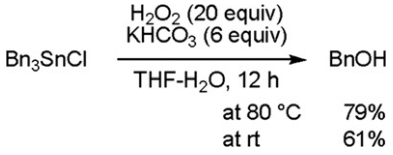
3. Conclusions

In conclusion we have demonstrated that Bn_3SnH is valuable as an easily accessible, removable organotin reagent for radical reduction of haloalkanes and radical cyclization of iodoalkenes. The tin byproducts formed can be removed by filtration and silica-gel column chromatography without any pretreatment. Bn_3SnH is more reactive toward homolytic hydrostannylation of alkynes than Bu_3SnH. The alkenylstannanes thus prepared serve as alkenyl donors in iodonolysis and Pd-catalyzed cross-coupling reactions. The removal of tin byproducts can be easily conducted also in these reactions. Additionally we have disclosed the hydrogen-donating ability of Bn_3SnH and the decomposability of Bn_3SnCl. This study has proved that introduction of a tribenzylstannyl group can improve the synthetic utility of organotin reagents.

4. Experimental

4.1. General experimental methods

Unless otherwise noted, all reactions and distillation of solvents were carried out under an argon atmosphere. Commercially available dry THF stored in a stainless container under an argon atmosphere was used as received. Hexane, dichloromethane, toluene, and benzene were dried by distillation from CaH_2. 1-Iodododecane (**1a**-I), 1-bromododecane (**1a**-Br), terminal alkynes (**6**), Bu_3SnH, and *t*-butyl acrylate were purchased from chemical companies and



Scheme 7. Decomposition of Bn_3SnCl.

simply distilled. Other commercially available organic and inorganic reagents were used as received. Organic halides **1b**-I [23], **1b**-Br [24], **1c** [25], **1d** [26], **1e** [26], **1f** [26], **3a** [26], **3b** [26], and **14** [19b], and enyne **9** [27] were prepared by the reported methods. The substrates prepared were purified by silica-gel column chromatography or distillation before their use. Analytical thin layer chromatography was performed using 0.25 mm silica-gel plates. Column chromatography was performed on silica-gel (spherical, neutral, 63–210 μm). ^{1}H (300, 400, or 500 MHz), ^{13}C NMR (75.0, 100, or 125.8 MHz), and ^{119}Sn NMR (186.5 MHz) were recorded in $CDCl_3$ or C_6D_6. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me_4Si), 7.15 ppm (C_6HD_5), or 7.26 ppm ($CHCl_3$) for the proton, at 77.0 ppm (centered on the signal of $CDCl_3$) or 128.0 ppm (centered on the signal of C_6D_6) for the carbon, and at 0.00 ppm (Me_4Sn) for the tin. Analytical GLPC was performed by a GC instrument equipped with a DB-1 capillary column (30 m × 0.25 mm) using nitrogen as carrier gas. High resolution mass was recorded on a MS instrument by EI method.

4.2. Synthesis of tribenzyltin hydride [12]

A solution of Bn_3SnCl (8.55 g, 20.0 mmol) [10] in THF (80 mL) was added to a suspension of $LiAlH_4$ (835 mg, 22.0 mmol) in Et_2O (20 mL) at 0 °C. After the addition of Bn_3SnCl, the mixture was stirred for 30 min. The reaction mixture was quenched with 20 wt% aqueous potassium sodium tartrate (100 mL) and extracted with Et_2O (3 × 40 mL). The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by flash column chromatography on silica-gel (hexane) gave the title compound (6.86 g, 17.4 mmol) in 87% yield. Rapid work-up and purification are required to prevent Bn_3SnH from decomposition. Mp 51–52 °C (hexane). ^{1}H NMR (C_6D_6) δ 2.17 (d, J = 1.5 Hz, ^2J (^{117,119}Sn–^{1}H) = 62 Hz, 6H), 5.71 (sept, J = 1.5 Hz, ^1J ($^{117/119}$Sn–^{1}H) = 1694/1772 Hz, 1H), 6.75–6.80 (m, 6H), 6.91–6.95 (m, 3H), 7.06–7.10 (m, 6H); ^{13}C NMR (C_6D_6) δ 17.8 (^1J ($^{117/119}$Sn–^{13}C) = 275/288 Hz), 124.2 (^5J (^{117,119}Sn–^{13}C) = 16 Hz), 127.7 (^3J (^{117,119}Sn–^{13}C) = 26 Hz), 128.9 (^4J (^{117,119}Sn–^{13}C) = 14 Hz), 142.0 (^2J (^{117,119}Sn–^{13}C) = 40 Hz); ^{119}Sn NMR (C_6D_6) δ −85.4 (d-sept, ^1J (^{119}Sn–^{1}H) = 1773 Hz, ^2J (^{119}Sn–^{1}H) = 62 Hz).

4.3. General procedure for radical reduction of haloalkanes

A haloalkane **1** (0.500 mmol) and Et_3B (1.0 M in hexane, 0.050 mL, 0.050 mmol) were added to a stirred mixture of Bn_3SnH (236 mg, 0.600 mmol) and hexane (2.0 mL) at room temperature. After 30 min CCl_4 (0.050 mL, 0.50 mmol) was added to the reaction mixture to convert the remaining Bn_3SnH into Bn_3SnCl. After 5 min the resultant mixture was filtered and evaporated. The crude product was purified by silica-gel column chromatography. In the reduction of **1a**-I and **1a**-Br, the yields of dodecane were determined by GC analysis of the crude product. The product was identified by comparison with the authentic sample in GC–MS analysis. Other isolated products were identified by ^{1}H and ^{13}C NMR analysis. The NMR data obtained well agree with the reported data (**2b** [28], **2d** [26], **2e** [29], and **2f** [26]) or the data of commercial samples (**2c**).

4.4. Radical cyclization of iodoalkenes *3a* and *3b*

A solution of Bn_3SnH (236 mg, 0.600 mmol) in CH_2Cl_2 (1.5 mL) was slowly added to a stirred mixture of **3a** or **3b** (0.500 mmol), Et_3B (1.0 M in hexane, 0.050 mL, 0.050 mmol), and CH_2Cl_2 (0.5 mL) over 15 min at room temperature. After completion of the radical cyclization, the reaction mixture was evaporated. The crude product was purified by silica-gel column chromatography. The isolated products were identified by ^{1}H and ^{13}C NMR analysis. The NMR data obtained well agree with the reported data [30].

4.5. Intermolecular radical addition of 1-iodododecane *1a*-I

A solution of Bn_3SnH (236 mg, 0.600 mmol) in toluene (1.5 mL) was slowly added to a stirred solution of **1a**-I (148 mg, 0.500 mmol), *t*-butyl acrylate (192 mg, 1.50 mmol), and Et_3B (1.0 M in hexane, 0.050 mL, 0.050 mmol) in toluene (0.5 mL) over 30 min at room temperature. After 1.5 h CCl_4 (0.10 mL, 1.0 mmol) was added to the reaction mixture. After 10 min undecane (72.4 mg) was added to the resultant mixture as an internal standard. The yield of dodecane and the recovery of **1a**-I were determined by GC analysis using a calibration curve (50% yield of dodecane; less than 5% recovery of **1a**-I). After evaporation of the reaction mixture, purification of the crude product by silica-gel column chromatography gave *t*-butyl pentadecanoate (**5**, 54 mg, 0.18 mmol) in 36% yield. The isolated product was identified by ^{1}H and ^{13}C NMR analysis. The NMR data obtained well agree with the reported data [19c]. The reaction using Bu_3SnH was performed by a similar method. The GC analysis of the reaction mixture showed that the yield of dodecane was 17%, and that the recovery of **1a**-I was 36%. The yield of **5** was determined to be 47% by ^{1}H NMR analysis of the crude mixture.

4.6. General procedure for homolytic hydrostannylation of alkynes

An alkyne **6** (0.500 mmol) and Et_3B (1.0 M in hexane, 0.050 mL, 0.050 mmol) were added to a stirred solution of Bn_3SnH (236 mg, 0.600 mmol) in toluene (2.0 mL) at room temperature. After a given reaction time, the reaction was quenched with CCl_4 (0.10 mL, 1.00 mmol) for 10 min. The resultant mixture was evaporated and purified by flash column chromatography on silica-gel. Since the stannylated products **7** are subject to protiodestannylation on silica-gel, the elution should be rapidly performed under an increased pressure.

4.6.1. 1-(Tribenzylstannyl)dodec-1-ene (*7a*, *E*:*Z* = 67:33)

Colorless oil. IR (neat) 2924, 2852, 1207, 754, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.87–0.91 (m, 3H) including 0.88 (t, J = 7.0 Hz, *Z*) and 0.89 (t, J = 6.5 Hz, *E*), 1.20–1.35 (m, 16H), 1.75–1.79 (m, 0.66H), 2.02–2.05 (m, 1.34H), 2.28 (s, ^2J ($^{117/119}$Sn–^{1}H) = 61.0/62.0 Hz, 4.02H, *E*), 2.31 (s, ^2J (^{117,119}Sn–^{1}H) = 61.0 Hz, 1.98H, *Z*), 5.52 (d, J = 12.0 Hz, 0.33H, *Z*), 5.59 (dt, J = 18.8, 1.0 Hz, 0.67H, *E*), 5.71 (dt, J = 18.8, 6.0 Hz, 0.67H, *E*), 6.47 (dt, J = 12.0, 7.0 Hz, 0.33H, *Z*), 6.83–6.86 (m, 6H), 6.98–7.01 (m, 3H), 7.13–7.18 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.1, 19.0 (^1J ($^{117/119}$Sn–^{13}C) = 273/285 Hz, *E*), 19.8 (*Z*), 22.67, 22.69, 28.6, 28.9, 29.0, 29.1, 29.33, 29.36, 29.46, 29.51, 29.53, 29.61, 29.63, 29.65, 31.89, 31.92, 33.8, 37.7, 123.45 (*E*), 123.54 (*Z*), 124.6 (*E*), 125.5 (*Z*), 127.39 (*Z*), 127.44 (*E*), 128.36 (*E*), 128.42 (*Z*), 141.7, 151.0 (*Z*), 152.1 (*E*). HRMS (EI$^+$) calcd for $C_{33}H_{44}Sn$ [M$^+$]: 560.2465. Found: 560.2455.

4.6.2. 6-(Tribenzylstannyl)hex-5-ene-1-ol (*7b*, *E*:*Z* = 64:36)

Colorless oil. IR (neat) 3300 (br s), 2933, 1207, 754, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.18 (t, J = 5.2 Hz, 1H), 1.25–1.50 (m, 4H), 1.72–1.78 (m, 0.72H, *Z*), 2.04–2.10 (m, 1.28H, *E*), 2.29 (s, ^2J (^{117,119}Sn–^{1}H) = 61.2 Hz, 3.84H, *E*), 2.32 (s, ^2J (^{117,119}Sn–^{1}H) = 60.8 Hz, 2.16H, *Z*), 3.56–3.65 (m, 2H), 5.42–5.77 (m, 1.64H) including 5.56 (d, J = 12.4 Hz, *Z*) and 5.61 (d, J = 19.0 Hz, *E*) and 5.68 (dt, J = 19.0, 5.6 Hz, *E*), 6.46 (dt, J = 12.4, 6.8 Hz, 0.36H, *Z*), 6.85 (d, J = 7.6 Hz, 6H), 6.98–7.02 (m, 3H), 7.14–7.18 (m, 6H); ^{13}C NMR ($CDCl_3$) δ19.0 (^1J ($^{117/119}$Sn–^{13}C) = 273/285 Hz, *E*), 19.7 (*Z*), 24.6 (*E*), 25.6 (*Z*), 31.9 (*E*), 32.3 (*Z*), 37.2, 62.6 (*Z*), 62.7 (*E*), 123.4 (*E*), 123.5 (*Z*), 125.2 (*E*), 125.9 (*Z*), 127.3 (*Z*), 127.4 (*E*), 128.3 (*E*), 128.4 (*Z*), 141.6, 150.4 (*Z*), 151.3 (*E*). HRMS (EI$^+$) calcd for $C_{27}H_{32}OSn$ [M$^+$]: 492.1475. Found: 492.1479.

*4.6.3. 1-Cyclohexyl-2-(tribenzylstannyl)ethene (**7c**, E:Z = 78:22)*

Colorless oil. IR (neat) 2922, 2848, 1207, 754, 696 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.95–1.27 (m, 5H), 1.45–1.50 (m, 0.44H), 1.60–1.72 (m, 4.78H), 1.85–1.93 (m, 0.78H, *E*), 2.28 (s, ^2J ($^{117/119}Sn-^1H$) = 61.0/62.0 Hz, 4.68H, *E*), 2.31 (s, ^2J ($^{117,119}Sn-^1H$) = 61.5 Hz, 1.32H, *Z*), 5.46 (d, *J* = 12.0 Hz, 0.22H, *Z*), 5.55 (dd, *J* = 19.0, 1.0 Hz, 0.78H, *E*), 5.64 (dd, *J* = 19.0, 6.0 Hz, 0.78H, *E*), 6.31 (dd, *J* = 12.0, 9.5 Hz, 0.22H, *Z*), 6.85 (d, *J* = 7.0 Hz, 6H), 6.98–7.02 (m, 3H), 7.13–7.17 (m, 6H); ^{13}C NMR ($CDCl_3$) δ19.0 (^1J ($^{117/119}Sn-^{13}C$) = 272/284 Hz, *E*), 19.9 (*Z*), 25.7 (*Z*), 25.8 (*Z*), 25.9 (*E*), 26.2 (*E*), 32.2 (*E*), 33.0 (*Z*), 45.0 (*E*), 47.4 (*Z*), 121.5 (*E*), 123.41 (*E*), 123.47 (*Z*), 123.54 (*Z*), 127.35 (*Z*), 127.42 (*E*), 128.3 (^4J ($^{117,119}Sn-^{13}C$) = 12.6 Hz, *E*), 128.4 (*Z*), 141.7 (^2J ($^{117,119}Sn-^{13}C$) = 37.7 Hz), 156.3 (*Z*), 157.4 (*E*). HRMS (EI^+) calcd for $C_{29}H_{34}Sn$ [M^+]: 502.1682. Found: 502.1695.

*4.6.4. 1-Phenyl-2-(tribenzylstannyl)ethene (**7d**, E:Z = 98:2)*

Yellow oil. IR (neat) 3024, 1597, 1493, 1452, 1205, 756, 729, 696 cm^{-1}. ^1H NMR ($CDCl_3$) for the *E*-isomer δ 2.39 (s, ^2J ($^{117/119}Sn-^1H$) = 61.0/62.0 Hz, 6H), 6.49 (s, ^2J ($^{117/119}Sn-^1H$) = 72.5/76.0 Hz, 2H), 6.89 (d, *J* = 7.0 Hz, 6H), 7.00–7.05 (m, 3H), 7.15–7.20 (m, 6H), 7.22–7.27 (m, 3H), 7.29–7.32 (m, 2H), resolved signals of the *Z*-isomer: δ 2.18 (s, 0.12H), 5.90 (d, *J* = 12.8 Hz, 0.02H), 7.63 (d, *J* = 12.8 Hz, 0.02H); ^{13}C NMR ($CDCl_3$) for the *E*-isomer δ 19.2 (^1J ($^{117/119}Sn-^{13}C$) = 278/291 Hz, three carbons), 123.6 (^5J ($^{117,119}Sn-^{13}C$) = 16.3 Hz, three carbons), 126.0 (two carbons), 126.6, 127.5 (^3J ($^{117,119}Sn-^{13}C$) = 25.0 Hz, six carbons), 127.9, 128.4 (two carbons), 128.5 (six carbons), 138.1, 141.3 (^2J ($^{117,119}Sn-^{13}C$) = 38.8 Hz, three carbons), 147.7 (^2J ($^{117,119}Sn-^{13}C$) = 11.3 Hz). HRMS (EI^+) calcd for $C_{29}H_{28}Sn$ [M^+]: 496.1213. Found: 496.1221.

*4.6.5. (E)-1-Tribenzylstannyl-2-(trimethylsilyl)ethene (**7e**, E:Z = >99:1)*

Colorless oil. IR (neat) 3022, 2952, 1491, 1246, 1205, 754, 696 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 2.30 (s, ^2J ($^{117,119}Sn-^1H$) = 60.0 Hz, 6H), 6.39 (d, *J* = 22.5 Hz, *J* ($^{117/119}Sn-^1H$) = 112/118 Hz, 1H), 6.61 (d, *J* = 22.5 Hz, *J* ($^{117/119}Sn-^1H$) = 120/126 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 6H), 6.98–7.02 (m, 3H), 7.13–7.18 (m, 6H); ^{13}C NMR ($CDCl_3$) δ-1.7 (three carbons), 18.9 (^1J ($^{117/119}Sn-^{13}C$) = 263/275 Hz, three carbons), 123.5 (^5J ($^{117,119}Sn-^{13}C$) = 15.0 Hz, three carbons), 127.5 (^3J ($^{117,119}Sn-^{13}C$) = 23.8 Hz, six carbons), 128.4 (^4J ($^{117,119}Sn-^{13}C$) = 12.5 Hz, six carbons), 141.6 (^2J ($^{117,119}Sn-^{13}C$) = 38.8 Hz, three carbons), 146.3, 157.6 (^1J ($^{117,119}Sn-^{13}C$) = 25.0 Hz). HRMS (EI^+) calcd for $C_{26}H_{32}SiSn$ [M^+]: 492.1295. Found: 492.1323.

4.7. General procedure for hydrostannylation of alkynes followed by iodonolysis

An alkyne **6** (0.500 mmol) and Et_3B (1.0 M in hexane, 0.050 mL, 0.050 mmol) were added to a stirred solution of Bn_3SnH (236 mg, 0.600 mmol) in toluene (2.0 mL) at room temperature. After a given reaction time, the reaction was quenched with I_2 (152 mg, 0.600 mmol) for 20 min. The resultant mixture was evaporated and purified by flash column chromatography on silica-gel. The isolated products **8** were identified by ^1H and ^{13}C NMR analysis. The NMR data well agree with the reported data (**8a** [31], **8b** [32], **8c** [33], and **8d** [34]).

*4.7.1. Diethyl 3-((E)-tribenzylstannylmethylene)-4-isopropylcyclopentane-1,1-dicarboxylate (**10**)*

Colorless oil. IR (neat) 2958, 1732, 1599, 1491, 1248, 1101, 756, 698 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.73 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.78–1.90 (m, 2H), 2.26–2.50 (m, 9H) including 2.33 (s), 2.71 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.11–4.26 (m, 4H), 5.34 (s, ^1J ($^{117,119}Sn-^1H$) = 79.4 Hz, 1H), 6.82 (d, *J* = 7.0 Hz, 6H), 6.97–7.02 (m, 3H), 7.11–7.17 (m, 6H); ^{13}C NMR ($CDCl_3$) δ13.90, 13.92, 16.7, 19.3 (^1J ($^{117/119}Sn-^{13}C$) = 273/285 Hz, three carbons), 21.0, 29.7, 34.1, 43.7 (^3J ($^{117,119}Sn-^{13}C$) = 32.7 Hz), 50.8 (^3J ($^{117,119}Sn-^{13}C$) = 55.3 Hz), 58.3, 61.25, 61.31, 116.7 (^1J ($^{117/119}Sn-^{13}C$) = 402/421 Hz), 123.4 (^5J ($^{117,119}Sn-^{13}C$) = 16.3 Hz, three carbons), 127.3 (^3J ($^{117,119}Sn-^{13}C$) = 23.9 Hz, six carbons), 128.3 (^4J ($^{117,119}Sn-^{13}C$) = 13.8 Hz, six carbons), 141.5 (^2J ($^{117,119}Sn-^{13}C$) = 37.7 Hz, three carbons), 162.3, 171.26, 171.31. HRMS (EI^+) calcd for $C_{36}H_{44}O_4Sn$ [M^+]: 660.2262. Found: 660.2271.

*4.7.2. Diethyl 3-((E)-iodomethylene)-4-isopropylcyclopentane-1,1-dicarboxylate (**11**)*

Colorless oil. IR (neat) 2960, 1732, 1464, 1367, 1252, 1190 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.83 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 1.23–1.29 (m, 6H), 1.87–2.07 (m, 2H), 2.54–2.63 (m, 2H), 2.75 (dt, *J* = 17.5, 2.5 Hz, 1H), 3.10 (dt, *J* = 17.5, 1.5 Hz, 1H), 4.17–4.24 (m, 4H), 5.88–5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ13.9 (two carbons), 16.9, 21.0, 29.3, 35.5, 45.7, 50.3, 57.5, 61.5, 61.6, 70.6, 153.9, 171.1, 171.2. HRMS (EI^+) calcd for $C_{15}H_{23}IO_4$ [M^+]: 394.0641. Found: 394.0619.

*4.8. Pd-catalyzed reaction of alkenylstannane (E)-**7d** with benzoyl chloride*

Benzoyl chloride (70.3 mg, 0.500 mmol) and (*E*)-**7d** (258 mg, 0.521 mmol) were added to a stirred solution of $Pd_2(dba)_3$ (7.0 mg, 0.0076 mmol) and Ph_3P (8.0 mg, 0.030 mmol) in THF (1.0 mL) at room temperature. After being stirred for 24 h, the reaction mixture was filtrated through a celite® pad and evaporated. Purification of the crude product by silica-gel column chromatography (hexane–AcOEt 10:1) gave chalcone (**12**, 94.5 mg, 0.454 mmol) in 91% yield. The NMR data well agree with the reported data [35].

*4.9. Pd-catalyzed reaction of alkenylstannane (E)-**7d** with p-iodotoluene*

Alkenylstannane (*E*)-**7d** (258 mg, 0.521 mmol) was added to a stirred mixture of *p*-iodotoluene (109 mg, 0.500 mmol), $Pd_2(dba)_3$ (7.0 mg, 0.0076 mmol), Ph_3P (8.0 mg, 0.030 mmol), CsF (152 mg, 1.00 mmol), and THF (1.0 mL) at room temperature. After being stirred for 24 h, the reaction mixture was filtrated through a celite® pad and evaporated. Purification of the crude product by silica-gel column chromatography (hexane) gave 1-methyl-4-((*E*)-2-phenylethenyl)benzene (**13**, 70.5 mg, 0.363 mmol) in 73% yield. The NMR data well agree with the reported data [36].

4.10. Radical clock experiment

7-Bromo-1,1-diphenylhept-1-ene (**14**, 75.7 mg, 0.230 mmol) was added to a stirred solution of AIBN (11.8 mg, 0.072 mmol) and Bn_3SnH (0.74 mL, 967 mg, 2.46 mmol) in benzene (10 mL at 20 °C, 10.77 mL at 80 °C). The mixture was heated to 80 °C and stirred for 10 h. Then CCl_4 (0.24 mL, 2.5 mmol) was added to the resultant mixture for conversion of the unreacted Bn_3SnH. After being stirred for 10 min, the reaction mixture was cooled to room temperature and evaporated. The molar ratio of 1,1-diphenyl-1-heptene (**15**) to (diphenylmethyl)cyclohexane (**16**) ([**15**]/[**16**]) was determined by ^1H NMR analysis of the crude product. The average ratio obtained by three runs ([**15**]/[**16**]: 1.64 (first run), 1.84 (second run), 1.71 (third run)) was 1.73. The rate constant k_H (Bn_3SnH) was calculated by the reported method ($k_H = 1.9 \times 10^7$) [19]. In the second run, the yields of **15** and **16** were estimated to be 46% and 25%, respectively, by ^1H NMR analysis using dibenzyl ether as the internal standard. The NMR data of isolated products well agree with the reported data [19,37].

4.11. Decomposition of tribenzylchlorostannane

Under the atmosphere, H_2O_2 (30 wt% in water, 2.0 mL, 20 mmol) was added to a stirred mixture of Bn_3SnCl (428 mg, 1.00 mmol), $KHCO_3$ (601 mg, 6.00 mmol), THF (10 mL), and water (3 mL). The mixture was heated to 80 °C and stirred for 12 h. After being cooled to room temperature, the resultant mixture was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with aqueous $Na_2S_2O_3$ (10 wt%, 20 mL) and dried over Na_2SO_4. To determine the yield of benzyl alcohol, the crude product was subjected to GC analysis using undecane as the internal standard.

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Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.11.007.

References

[1] A.G. Davies, J. Chem. Res. (2006) 141–148.
[2] A.J. Clark, in: M. Maloney (Ed.), Science of Synthesis, vol. 5, Georg Thieme Verlag, Stuttgart, 2003, pp. 205–271.
[3] A.G. Davies, Organotin Chemistry, Wiley-VCH, Weinheim, 2004.
[4] M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987.
[5] (a) P. Renaud, M.P. Sibi (Eds.), Radicals in Organic Synthesis, Wiley-VCH, Weinheim, 2001;
(b) D.P. Curran, N.A. Porter, B. Giese, Stereochemistry of Radical Reactions, VCH, Weinheim, 1996;
(c) D.P. Curran, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, Oxford, 1991, pp. 715–831. Chapters 4.1–4.2;
(d) B. Giese, Radicals in Organic Synthesis, Formation of Carbon–Carbon Bonds, Pergamon Press, Oxford, 1986.
[6] (a) K. Miura, D. Wang, A. Hosomi, J. Am. Chem. Soc. 127 (2005) 9366–9367;
(b) K. Miura, D. Wang, Y. Matsumoto, A. Hosomi, Org. Lett. 7 (2005) 503–505;
(c) P. Dimopoulos, A. Athlan, S. Manaviazar, J. George, M. Walters, L. Lazarides, A.E. Aliev, K.J. Hale, Org. Lett. 7 (2005) 5369–5372.
[7] (a) M. Kosugi, K. Fugami, in: E. Negishi, A. de Meijere (Eds.), Organopalladium Chemistry for Organic Synthesis, vol. 1, Wiley, New York, 2002, pp. 263–285;
(b) T.N. Mitchell, in: A. de Meijere, A.F. Diederich (Eds.), Metal-Catalyzed Cross-coupling Reactions, second ed., Wiley-VCH, Weinheim, 2004, pp. 125–162.
[8] A. Crombie, S.-Y. Kim, S. Hadida, D.P. Curran, Org. Synth. 79 (2002) 1–10.
[9] M. Nath, Appl. Organomet. Chem. 22 (2008) 598–612.
[10] P. Boudjouk, D.J. Seidler, D. Grier, G.J. McCarthy, Chem. Mater. 8 (1996) 1189–1196.
[11] A.E. Finholt, A.C. Bond Jr., K.E. Wilzbach, H.I. Schlesinger, J. Am. Chem. Soc. 69 (1947) 2692–2696.
[12] A.B. Chopa, L.C. Koll, J.C. Podesta, F.G. Thorpe, Synthesis (1983). 722–722.
[13] K. Miura, Y. Ichinose, K. Nozaki, K. Fugami, K. Oshima, K. Utimoto, Bull. Chem. Soc. Jpn. 62 (1989) 143–147.
[14] K. Nozaki, K. Oshima, K. Utimoto, J. Am. Chem. Soc. 109 (1987) 2547–2549.
[15] Y. Ren, J. Jun, L. Yu, M. Li, X. Yang, B. Wan, H. Chen, Syn. React. Inorg. Metal-Org. Chem. 34 (2004) 565–572 (and references therein).
[16] (a) M. Taniguchi, K. Nozaki, K. Miura, K. Oshima, K. Utimoto, Bull. Chem. Soc. Jpn. 65 (1992) 349–353;
(b) A.J. Leusink, H.A. Budding, W. Drenth, J. Organomet. Chem. 11 (1968) 541–550.
[17] R. Mook Jr., P.M. Sher, Org. Synth. 66 (1988) 75–86.
[18] M. Newcomb, in: P. Renaud, M.P. Sibi (Eds.), Radicals in Organic Synthesis, vol. 1, Wiley-VCH, Weinheim, 2001, pp. 317–336.
[19] (a) M. Newcomb, J.H. Horner, M.A. Filipkowski, C. Ha, S.-U. Park, J. Am. Chem. Soc. 117 (1995) 3674–3684;
(b) G. Gualtieri, S.J. Geib, D.P. Curran, J. Org. Chem. 68 (2003) 5013–5019;
(c) K. Miura, K. Ootsuka, A. Hosomi, Synlett (2005) 3151–3153.
[20] C. Chatgilialoglu, M. Newcomb, Adv. Organomet. Chem. 44 (1999) 67–112.
[21] MSDS provided by Alfa Aesar® via the Internet at http://www.alfa.com.
[22] K. Tamao, N. Ishida, J. Organomet. Chem. 269 (1984) C37–C39.
[23] R.W. Bates, M.R. Dewey, Org. Lett. 11 (2009) 3706–3708.
[24] S.J. Coles, J.F. Costello, W.N. Draffin, M.B. Hursthouse, S.P. Paver, Tetrahedron 61 (2005) 4447–4452.
[25] W.-C. Zhang, C.-J. Li, J. Org. Chem. 65 (2000) 5831–5833.
[26] K. Miura, M. Tomita, Y. Yamada, A. Hosomi, J. Org. Chem. 72 (2007) 787–792.
[27] R. Garcia-Fandino, E.M. Codesido, E. Sobarzo-Sánchez, L. Castedo, J.R. Granja, Org. Lett. 6 (2004) 193–196.
[28] L.-A. Chen, K. Sung, Org. Lett. 11 (2009) 3370–3373.
[29] (a) K. Fujita, C. Asai, T. Yamaguchi, F. Hanasaka, R. Yamaguchi, Org. Lett. 7 (2005) 4017–4019;
(b) B.H. Lipshutz, R.S. Wilhelm, J.A. Kozlowski, D. Parker, J. Org. Chem. Soc. 49 (1984) 3928–3938.
[30] K. Takami, S. Mikami, H. Yorimitsu, H. Shinokubo, K. Oshima, Tetrahedron 59 (2003) 6627–6635.
[31] A. Takács, P. Ács, R. Farkas, G. Kokotos, L. Kollár, Tetrahedron 64 (2008) 9874–9878.
[32] A. Nisida, F. Shirato, M. Nakagawa, Tetrahedron: Asymmetry 11 (2000) 3789–3805.
[33] S.A. Batsanov, J.P. Knowles, B. Samsam, A. Whiting, Adv. Synth. Catal. 350 (2008) 227–233.
[34] (a) J.J. Mousseau, J.A. Bull, A.B. Charette, Angew. Chem. Int. Ed. 49 (2010) 1115–1118;
(b) A. Carpita, A. Ribecai, R. Rossi, P. Stabile, Tetrahedron 58 (2002) 3673–3680.
[35] F. Fang, Y. Li, S.-K. Tian, Eur. J. Org. Chem. (2011) 1084–1091.
[36] P. Srinivas, K. Srinivas, P.R. Likhar, B. Sridhar, K.V. Mohan, S. Bhargava, M.L. Kantam, J. Organomet. Chem. 696 (2011) 795–801.
[37] M.F. Semmelhack, J.W. Herndon, Organometallics 2 (1983) 363–372.