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REGIO- AND STEREO-SELECTIVE SYNTHESIS OF VINYLSTANNANES. TRANSITION-METAL CATALYZED STANNYLMETALATION OF ACETYLENES AND CONVERSION OF ENOL TRIFLATES AND VINYL IODIDES INTO VINYLSTANNANES

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Summary

Two new methods for the regio- and stereo-selective synthesis of vinylstannanes are described. (i) The reaction of terminal acetylenes with n-$Bu_3SnMgMe$, n-$Bu_3SnAlEt_2$, or $(n\text{-}Bu_3Sn)_2Zn$ in the presence of various transition-metal catalysts provides vinylstannanes in good yields. Whereas copper-catalyzed stannylmagnesation of 4-benzyloxy-1-butyne gives (*E*)-4-benzyloxy-1-tributylstannyl-1-butene exclusively, palladium-catalyzed stannylzincation affords 4-benzyloxy-2-tributylstannyl-1-butene preferentially. (ii) Treatment of enol triflates or vinyl iodide with Me_3Sn-MgMe in the presence of CuCN catalyst gives vinylstannanes in good yields.

Introduction

The synthetic utility [1] of vinylstannanes is critically dependent on their availability. The hydrostannation of acetylenes is the simplest and most direct route to vinylstannanes. This reaction, however, is generally not highly stereoselective [2]. *trans*-Addition predominates under kinetic conditions, whereas *cis*-addition products tend to predominate under thermodynamic conditions. Although several other preparative routes [3] are now available, there still exists a need for new methods which have generality and high regio- and stereo-selectivity. Here we describe two new methods for the selective synthesis of vinylstannanes: (i) transition-metal catalyzed stannylmetalation of acetylenes; and (ii) transformation of enol triflates or vinyl iodides into vinylstannanes with Me_3Sn-MgMe in the presence of CuCN catalyst.

Results and discussion

(i) Regioselective stannylmetalation of acetylenes in the presence of a transition-metal catalyst [4]

The reaction of the organometallic compounds prepared from $PhMe_2SiLi$ and

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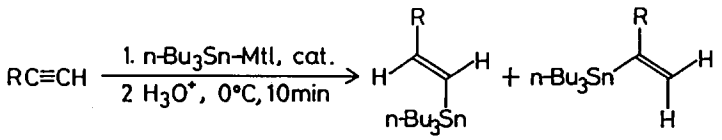
MeMgI or Et_2AlCl with an acetylenic linkage affords simple and general access to the *cis*-addition products of the component atoms. The regio- and stereo-chemistry depend greatly on the nature of the transition-metal catalysts and the reaction is useful in synthetic work [5]. Further extension of this method to stannic reagents derived from n-Bu_3SnLi [6] and MeMgI, Et_2AlCl, or $ZnBr_2$ has provided us with a novel route to vinylstannanes under good control of the regio- and stereoselectivity.

Treatment of 4-benzyloxy-1-butyne with n-$Bu_3SnMgMe$, generated from n-Bu_3SnLi and MeMgI, in the presence of a catalytic amount of CuCN gave (*E*)-4-benzyloxy-1-tributylstannyl-1-butene as the single product [7,8]. Representative results are summarized in Table 1. Many combinations of n-Bu_3Sn-metal and transition-metal catalysts were examined. Whereas the n-$Bu_3SnAlEt_2$ and CuCN system provided a mixture of (*E*)-1-tributylstannyl-1-alkene (**1**) and its regio-isomer (**2**) in an 81/19 ratio (entry 4 in Table 1), $(n\text{-}Bu_3Sn)_2Zn$ and $Pd(PPh_3)_4$ gave **2** predominantly (entry 6 in Table 1).

The reaction of n-$Bu_3SnMgMe$ and CuCN with an internal acetylene such as 5-benzyloxy-2-pentyne gave no addition product and the starting acetylenic compound was recovered unchanged. As shown in Scheme 1, stannylmetalation proceeds in a *cis*-fashion. Treatment of phenylacetylene with n-$Bu_3SnAlEt_2$ in the presence

TABLE 1

TRANSITION-METAL CATALYZED STANNYLMETALATION [a]



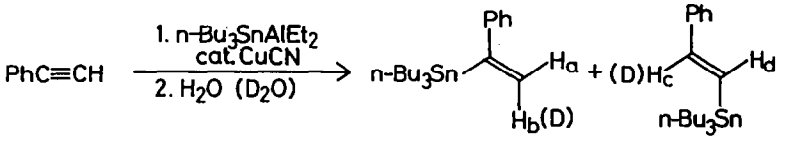
1 **2**

Entry	Substrate	Reagent	Catalyst	Yield [b] (%)	Ratio [c] of **1**/**2**	
					1	**2**
1	R = $PhCH_2OCH_2CH_2$	$(n\text{-}Bu_3Sn)_2CuCN$ [d]		75	36	64
2		n-$Bu_3SnMgMe$ [e]	CuCN	88	100	0
3		n-$Bu_3SnMgMe$	$CuBr\cdot SMe_2$	23	34	66
4		n-$Bu_3SnAlEt_2$ [e]	CuCN	86	81	19
5		$(n\text{-}Bu_3Sn)_2Zn$ [f]	CuCN	63	26	74
6		$(n\text{-}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	81	14	86
7	R = Ph	n-$Bu_3SnMgMe$	CuCN	89 [g]	> 95	< 5
8		n-$Bu_3SnAlEt_2$	CuCN	88 [g]	79	21
9		$(n\text{-}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	93 [g]	60	40
10		$(n\text{-}Bu_3Sn)_2Zn$	$PdCl_2(PPh_3)_2$	89 [g]	> 95	< 5
11	R = $n\text{-}C_{10}H_{21}$	n-$Bu_3SnMgMe$	CuCN	70 [h]	70	30
12		n-$Bu_3SnAlEt_2$	CuCN	87 [h]	38	62
13		$(n\text{-}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	70 [h]	< 5	> 95

[a] 3 mmol of n-Bu_3Sn-Mtl reagent, 1 mmol of acetylene compound, and 5 mol% of catalyst were employed. [b] Isolated yield unless otherwise noted. [c] The ratios were determined by GLPC and ^1H NMR spectra. [d] A reagent was produced by mixing the stannyllithium with CuCN in a 2/1 ratio (see ref. 7). [e] Prepared from the stannyllithium and MeMgI (or Et_2AlCl) in a 1/1 ratio. [f] Prepared from the stannyllithium and $ZnBr_2$ in a 2/1 ratio. [g] GLPC yield using n-hexacosane as the internal standard. [h] ^1H NMR yield using dimethyl sulfoxide as the internal standard.

of CuCN gave two isomers which were separated by preparative GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 200°C). The product **3** (t_r 4 min) showed ^{1}H NMR ($CDCl_3$) signals at δ 5.43 (d, J 2.7 Hz, H_b), 6.03 (d, J 2.7 Hz, H_a). The other isomer, **4**, having a longer retention time (t_r 7 min) gave ^{1}H NMR ($CDCl_3$) absorption at δ 6.87 (bs, 2H, H_c and H_d). Assignment of the stereochemistry of H_a and H_b was based on the ^{1}H NMR spectral data of the hydrostannation products [9]. Quenching the reaction mixture with D_2O provided an isomeric mixture whose ^{1}H NMR spectrum showed only two signals in the olefinic region at δ 5.98 and 6.82. The disappearance of the higher field signal at δ 5.43 in the spectrum of compound **3** is also consistent with a *cis*-addition process.

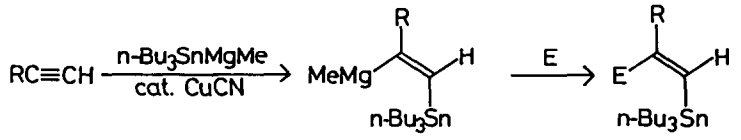
SCHEME 1



(3) **(4)**

The new reaction has provided not only simple vinylstannanes but also functionalized alkenylstannanes on treatment of an intermediary alkenylmetal species with various electrophiles. For instance, stannylmagnesation of 4-benzyloxy-1-butyne catalyzed by CuCN followed by the addition of MeI (large excess) gave **5b** in 69% yield (Scheme 2).

SCHEME 2



(5a-5e)

R = $PhCH_2OCH_2CH_2$

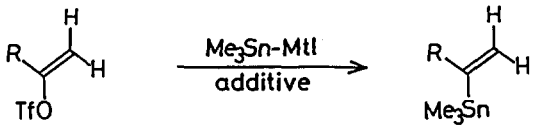
a, E = H (H_2O, 88 %); **d**, E = Allyl (CH_2=$CHCH_2Br$, 78 %);
b, E = Me (MeI, 69 %); **e**, E = PhCH(OH) (PhCHO, 65 %))
c, E = Et (EtI, 73 %);

(ii) Conversion of enol triflates and vinyl iodides into vinylstannanes with Me_3Sn-MgMe

In the last decade, cross-coupling of alkenyl halides with organolithium or organomagnesium compounds has been achieved in the presence of a Pd^0 or Ni^0 catalyst [10]. Recently, we reported the coupling reactions of enol phosphates with R_3Al in the presence of $Pd(PPh_3)_4$ catalyst [11] and the application of the reaction to vinylsilane synthesis by means of $PhMe_2SiAlEt_2$ instead of the trialkylaluminium reagent [12]. Further extension of this approach to the synthesis of vinylstannanes has been studied. The treatment of enol phosphates with $R_3SnAlEt_2$ in the presence

TABLE 2

CONVERSION OF ENOL TRIFLATES INTO VINYLSTANNANES [a]



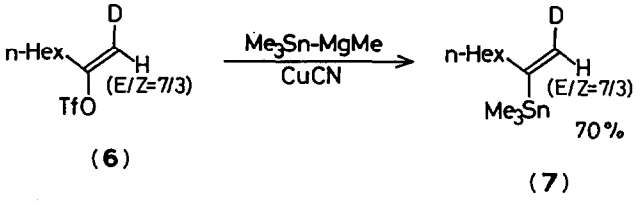
Run	R	Mtl	Additive	Yield (%) [b]
1	n-C_6H_{13}	$AlEt_2$	$Pd(PPh_3)_4$ [c]	10
2	n-C_6H_{13}	MgMe	–	0
3	n-C_6H_{13}	Li	CuCN [d]	0
4	n-C_6H_{13}	MgMe	CuCN	70
5	Cyclohexyl	MgMe	CuCN	56
6	Ph	MgMe	CuCN	40

[a] 2 mmol of Me_3Sn-Mtl reagent and 1 mmol of enol triflate were employed. [b] GLPC yield. See Experimental section. [c] 0.1 mmol of Pd^0 was used. [d] 0.3 mmol of CuCN was added.

of $Pd(PPh_3)_4$ catalyst gave no desired vinylstannanes. However, the palladium(0) catalyzed reaction of enol triflates [13,14] with $Me_3SnAlEt_2$ gave the desired vinylstannane, although the yield was poor (run 1 in Table 2). In order to improve the yield of vinylstannane, several combinations of trialkylstannyl metal reagents and transition-metal catalysts were examined. Among them, the $Me_3SnMgMe$ and CuCN system gave the desired vinylstannanes in good yields (run 4 in Table 2). In the case of R = Ph in Table 2, the yield of vinylstannane was low, since the methyl group on magnesium competed with the Me_3Sn moiety to give α-methylstyrene as a by-product in 40% yield in addition to the desired vinylstannane.

As shown in Scheme 3, the reaction proceeded with high stereospecificity. Treatment of 1-deuterio-2-trifluoromethanesulfonyloxy-1-octene (**6**, $E/Z = 7/3$), which was derived from 1-deuterio-1-octyne and trifluoromethanesulfonic acid [15], with $Me_3SnMgMe$ and CuCN gave the corresponding isomeric mixture of vinylstannanes (**7**, $E/Z = 7/3$).

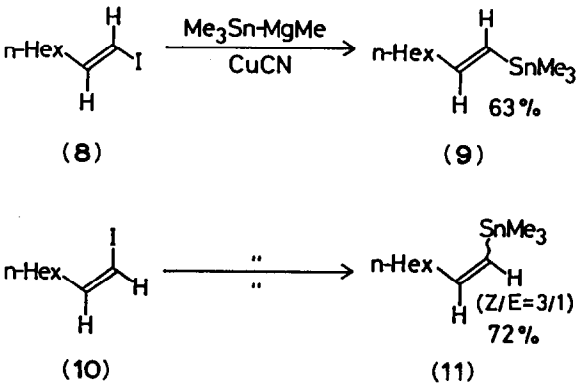
SCHEME 3



(**6**) (**7**)

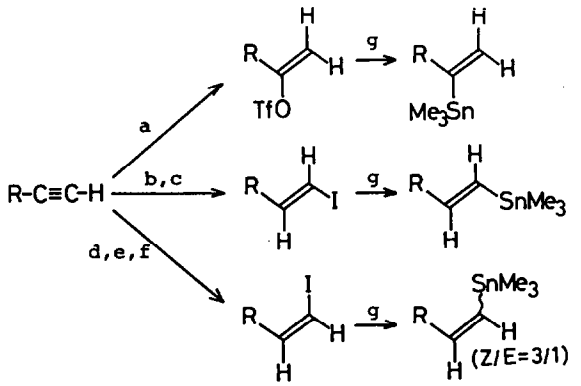
Vinyl iodides could also be transformed into vinylstannane with the $Me_3SnMgMe$ and CuCN system. The nature of the substrates affects the stereochemical results slightly. Whereas (*E*)-1-iodo-1-octene (**8**) gave (*E*)-trimethylstannyl-1-octene (**9**) exclusively, the (*Z*)-isomer (**10**) provided (*Z*)-vinylstannane (**11**) stereoselectively, contaminated with the (*E*)-isomer (Scheme 4).

SCHEME 4



Each starting material, 2-trifluoromethanesulfonyloxy-1-octene, (*E*)-1-iodo-1-octene [16], or (*Z*)-1-iodo-1-octene [17], can be easily obtained from 1-octyne, thus the present new method provides us with a simple and versatile route for the stereo- and regio-selective synthesis of vinylstannanes starting from 1-alkynes (Scheme 5).

SCHEME 5



a: TfOH in pentane, b: DIBAL in hexane, c: I_2, d: n-BuLi, Me_3SiCl, e: DIBAL in ether/hexane, f: I_2, g: Me_3Sn-MgMe, CuCN

TABLE 3

^{119}Sn NMR SPECTRAL DATA OF VINYLSTANNANES [a,b]

Run	R	R'	R'_3Sn, H, R, H	H, SnR'_3, R, H	H, H, R, SnR'_3
1	$PhCH_2OCH_2CH_2$	n-Bu	−45.2	−51.8	–
2	n-Hex	Me	−35.7	−40.7	−58.3
3	Ph	n-Bu	−39.7	−44.6	−57.3
4	Ph	Me	−28.0	−32.4	−51.3
5	Cyclohexyl	Me	−35.9	−38.2	−57.9

[a] All spectra were measured in $CDCl_3$. The chemical shifts are given in δ (ppm) with tetramethylstannane as the internal standard. [b] See ref. 19.

The ^{119}Sn NMR spectra are very useful for determination of the stereochemistry [18]. The chemical shifts of vinylstannanes which have different substitution patterns are summarized in Table 3. The ratio of isomeric mixtures can be easily measured by integrating the peak area of the corresponding signals.

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer, the mass spectra on a Hitachi M-80 machine, the proton NMR spectra on a Varian EM-390 spectrometer and a Varian XL-200 spectrometer, and the ^{119}Sn-NMR spectra on a JEOL JNM-FX 90Q spectrometer. The chemical shifts of the proton NMR are given in δ (ppm), with tetramethylsilane as the internal standard; those of the ^{119}Sn NMR are given in δ (ppm), with tetramethylstannane as the internal standard. The analyses were carried out by the staff of the Elemental Analyses Center, Kyoto University. Tetrahydrofuran was freshly distilled from sodium ketyl benzophenone. Purification of products was performed by column chromatography on silica-gel (Wakogel C-100), alumina (Merck, Art. 1077 Aluminiumoxid 90 aktiv neutral, 70–230 mesh) or by preparative thin-layer chromatography (TLC). Analytical GLPC was performed with a Shimadzu GC-4CPT.

(E)-4-Benzyloxy-1-tributylstannyl-1-butene

A hexane solution of butyllithium (1.5 *M*, 6.0 ml, 9.0 mmol) was added to a suspension of anhydrous tin(II) chloride (0.58 g, 3.0 mmol) in THF (4 ml) at 0°C. After stirring for 20 min, the reaction mixture was treated with an ethereal solution of methylmagnesium iodide (1.0 *M*, 3.0 ml, 3.0 mmol) at 0°C. After the resulting mixture had been stirred for 15 min, CuCN (4 mg, 5 mol%) and 4-benzyloxy-1-butyne (0.16 g, 1.0 mmol) in THF (5 ml) were added successively, and the whole was stirred for 30 min at 0°C. The reaction mixture was poured into a saturated NH_4Cl aqueous solution (20 ml) and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated. Purification by alumina column chromatography gave pure 4-benzyloxy-1-tributylstannyl-1-butene (0.38 g, 88% yield) as a colorless oil: b.p. 125°C (bath temp., 0.1 Torr); IR (neat): 1590, 1460, 1450, 1100, 990, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.1 (m, 15H), 1.2–1.7 (m, 12H), 2.4–2.6 (m, 2H), 3.55 (t, *J* 7.0 Hz, 2H), 4.55 (s, 2H), 6.00 (s, 2H), 7.3–7.4 (m, 5H); Found: C, 61.29; H, 8.96. $C_{23}H_{40}OSn$ calcd.: C, 61.22; H, 8.93%.

4-Benzyloxy-2-tributylstannyl-1-butene

Anhydrous zinc(II) bromide (0.45 g, 2 mmol) was added to tributylstannyllithium (4.0 mmol), which was prepared by treating tributylstannane (1.2 g, 4.0 mmol) with a THF solution of lithium diisopropylamide (0.5 *M*, 8.0 ml, 4.0 mmol). The mixture was stirred for 20 min at 0°C under an argon atmosphere, then $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added to the resulting mixture. After being stirred for 5 min, a solution of 4-benzyloxy-1-butyne (0.16 g, 1.0 mmol) in THF (5 ml) was added, and the whole was stirred for 3 h at 0°C. The reaction mixture was poured into a saturated NH_4Cl aqueous solution (20 ml) and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated. Purification by alumina column chromatography gave a mixture of

4-benzyloxy-2-tributylstannyl-1-butene (**12**) and (*E*)-4-benzyloxy-1-tributylstannyl-1-butene (**13**) in an 81% combined yield. GLPC analysis (Silicone OV 17 3% on Uniport HP, 2 m, 200°C) showed two peaks having retention times at 9 (**12**) and 11 min (**13**) in an 86/14 ratio. Separation by preparative GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 200°C) gave pure **12** as a colorless oil: b.p. 120°C (bath temp., 0.1 Torr); IR (neat): 2950, 1460, 1100, 910, 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.1 (m, 15H), 1.2–1.7 (m, 12H), 2.48 (t, *J* 6 Hz, 2H), 3.87 (t, *J* 6 Hz, 2H), 4.38 (s, 2H) 5.1–5.2 (m, 1H), 5.6–5.7 (m, 1H), 7.1–7.2 (m, 5H); Found: C, 61.13; H, 9.02 $C_{23}H_{40}OSn$ calcd.: C, 61.22, H, 8.93%.

*(E)-1-Phenyl-2-tributylstannylethene (**14**) [20]*

The title compound was obtained on treatment of phenylacetylene with th n-$Bu_3SnMgMe$ and CuCN system: b.p. 140°C (bath temp., 0.1 Torr); IR (neat 2870, 1580, 1560, 1490, 1060, 980, 960, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.9–1.0 (n 15H), 1.3–1.5 (m, 12H), 6.87 (bs, 2H), 6.9–7.4 (m, 5H).

1-Phenyl-1-tributylstannylethene [20]

Treatment of phenylacetylene with $(n\text{-}Bu_3Sn)_2Zn$ and $Pd(PPh_3)_4$ gave a mixture of (*E*)-1-phenyl-2-tributylstannylethene (**14**) and 1-phenyl-1-tributylstannylethene (**15**). GLPC analysis (Silicone OV 17 3% on Uniport HP, 2 m, 200°C) showed two peaks having retention times at 4 (**14**) and 7 min (**15**) in a 60/40 ratio. Separation by preparative GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 200°C) gave pure vinylstannane **15** as a colorless oil: b.p. 135°C (bath temp., 1 Torr); IR (neat): 2870, 1590, 1480, 1020, 870 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 15H), 1.2–1.5 (m, 12H), 5.43 (d, *J* 3 Hz, 1H), 6.02 (d, *J* 3 Hz, 1H), 7.2–7.3 (m, 5H).

(E)-4-Benzyloxy-2-methyl-1-tributylstannyl-1-butene

4-Benzyloxy-1-butyne (0.16 g, 1.0 mmol) was treated with the n-$Bu_3SnMgMe$ (3 mmol) and CuCN (0.05 mmol) reagent as described for the preparation of (*E*)-4-benzyloxy-1-tributylstannyl-1-butene. The mixture was stirred for 2 min after the addition of 4-benzyloxy-1-butyne, and iodomethane (1 ml) was added in one portion. After being stirred for 20 min, the reaction mixture was poured into a saturated NH_4Cl aqueous solution, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by alumina column chromatography gave 4-benzyloxy-2-methyl-1-tributylstannyl-1-butene in 69% yield (0.32 g) as a colorless oil: b.p. 150°C (bath temp., 1 Torr); IR (neat): 2900, 1600, 1490, 1100, 1030, 870 cm^{-1}; ^1H NMR ($CDCl_3$): 0.8–0.9 (m, 15H), 1.2–1.6 (m, 12H), 1.78 (s, 3H), 2.47 (t, *J* 8 Hz, 2H), 3.60 (t, *J* 8 Hz, 2H), 4.53 (s, 2H), 5.52 (s, 1H), 7.3–7.4 (m, 5H); ^{119}Sn NMR ($CDCl_3$): δ −62.1; Found: *m/z* 407.1600. $C_{20}H_{33}O^{118}Sn$ calcd.: ($M - C_4H_9$) 407.1551.

(E)-4-Benzyloxy-2-ethyl-1-tributylstannyl-1-butene

B.p. 165°C (bath temp., 1 Torr); IR (neat): 2860, 1590, 1490, 1110, 1020, 860 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–0.95 (m, 15H), 1.03 (t, *J* 8 Hz, 3H), 1.2–1.6 (m, 12H), 2.07 (q, *J* 8 Hz, 2H), 2.48 (t, *J* 6 Hz, 2H), 3.59 (t, *J* 6 Hz, 2H), 4.53 (s, 2H), 5.48 (s, 1H), 7.3–7.4 (m, 5H); ^{119}Sn NMR ($CDCl_3$): δ −63.1; Found: C, 62.61; H, 9.25. $C_{25}H_{44}OSn$ calcd.: C, 62.65; H, 9.25%.

(E)-4-Benzyloxy-2-(2-propenyl)-1-tributylstannyl-1-butene

B.p. 175°C (bath temp., 1 Torr); IR (neat): 2900, 1620, 1590, 1490, 1100, 1010, 990, 910, 870 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–0.9 (m, 15H), 1.2–1.6 (m, 12H), 2.46 (t, J 7 Hz, 2H), 2.81 (d, J 7 Hz, 2H), 3.59 (t, J 7 Hz, 2H), 4.52 (s, 2H), 5.02 (d, J 10 Hz, 1H), 5.05 (d, J 18 Hz, 1H), 5.61 (s, 1H), 5.75 (ddt, J 18, 10, 7 Hz, 1H), 7.2–7.3 (m, 5H); ^{119}Sn NMR ($CDCl_3$): δ −62.6; Found: m/z 433.1764. $C_{22}H_{35}O^{118}Sn$ calcd.: ($M - C_4H_9$) 433.1707.

(E)-4-Benzyloxy-2-hydroxyphenylmethyl-1-tributylstannyl-1-butene

This compound was obtained by the same procedure as that for (*E*)-4-benzyloxy-2-methyl-1-tributylstannyl-1-butene. Instead of iodomethane, benzaldehyde (0.31 g, 3 mmol) was added to the reaction mixture at −78°C in one portion: decomp. 180°C (bath temp., 0.15 Torr); IR (neat): 3360, 1690, 1590, 1490, 1020, 870 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 15H), 1.2–1.6 (m, 12H), 2.1–2.3 (m, 2H), 3.4–3.6 (m, 2H), 3,67 (d, J 4 Hz, 1H), 4.50 (s, 2H), 5.18 (d, J 4 Hz, 1H), 5.93 (s, 1H), 7.2–7.5 (m, 10H); ^{119}Sn NMR ($CDCl_3$): δ −63.4; Found: m/z 497.1773. $C_{26}H_{37}O_2{}^{118}Sn$ calcd.: ($M - C_4H_9$) 497.1816.

2-Trifluoromethanesulfonyloxy-1-octene

This compound was produced from 1-octyne and trifluoromethanesulfonic acid according to the reported procedure [15]. Both 1-cyclohexyl-1-trifluoromethanesulfonyloxyethene and 1-phenyl-1-trifluoromethanesulfonyloxyethene were produced in the same manner.

(E)-1-Iodo-1-octene

The title compound was obtained from the hydroalumination of 1-octyne and the continuous treatment of iodine according to the reported procedure [16].

(Z)-1-Iodo-1-octene

This compound was produced from the hydroalumination of 1-trimethylsilyl-1-octyne in ethereal solution and the continuous treatment of iodine following the reported procedure [17,21].

General procedure for the coupling reaction of $R_3SnMgMe$ with enol triflates or vinyl iodides

The transformation of 2-trifluoromethanesulfonyloxy-1-octene into 2-trimethylstannyl-1-octene is taken as representative. An ethereal solution of methyllithium (1.5 *M*, 4.0 ml, 6.0 mmol) was added to a suspension of anhydrous tin(II) chloride (0.38 g, 2.0 mmol) in THF (5 ml) at 0°C. The reaction mixture was stirred for 20 min and treated with an ethereal solution of methylmagnesium iodide (1.0 *M*, 2.0 ml, 2.0 mmol) at 0°C. After the resulting mixture had been stirred for 15 min, CuCN (27 mg, 0.3 mmol) and a solution of 2-trifluoromethanesulfonyloxy-1-octene (0.26 g, 1 mmol) in THF (3 ml) were added successively, and the whole was stirred for 5 h at room temperature. The reaction mixture was poured into a saturated NH_4Cl aqueous solution (20 ml) and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated. Purification by silica-gel column chromatography gave 2-trimethylstannyl-1-octene as a colorless oil (0.23 g) which was contaminated with a trace amount of unidentified

impurities. The yield (70%) of vinylstannane was determined by GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 110°C) using hexadecane as the internal standard. B.p. 80°C (bath temp., 8 Torr); IR (neat): 2870, 1460, 1180, 905, 760 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.12 (s, 9H), 0.87 (t, J 6 Hz, 3H), 1.27 (bs, 8H), 2.28 (t, J 7 Hz, 2H), 5.12 (bs, 1H), 5.63 (bs, 1H); Found: C, 48.05; H, 8.90. $C_{11}H_{24}Sn$ calcd.: C, 48.04; H, 8.80%.

1-Deuterio-2-trimethylstannyl-1-octene

Treatment of 1-deuterio-2-trifluoromethanesulfonyloxy-1-octene ($E/Z = 7/3$) derived from 1-deuterio-1-octyne and trifluoromethanesulfonic acid [15] with the $Me_3SnMgMe$-CuCN system gave the 1-deuterio-2-trimethylstannyl-1-octenes as a stereoisomeric mixture ($E/Z = 7/3$). The E/Z ratio was determined by the absorption of olefinic protons at δ 5.12 for the E-isomer and δ 5.63 for the Z-isomer: ^{119}Sn NMR ($CDCl_3$): δ −35.6 (J(Sn–D) 23.7 Hz for the E-isomer and 11.3 Hz for the Z-isomer).

1-Cyclohexyl-1-trimethylstannylethene

A 54% yield was determined by GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 130°C) using hexadecane as the internal standard. B.p. 105°C (bath temp., 6 Torr); IR (neat): 2950, 2870, 1440, 1080, 905 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.13 (s, 9H), 1.10–1.45 (m, 6H), 1.55–1.85 (m, 4H), 2.05–2.25 (m, 1H), 5.08 (dd, J 2.5, 0.8 Hz, 1H), 5.64 (dd, J 2.5, 1.2 Hz, 1H); Found: C, 48.31, H, 8.32. $C_{11}H_{22}Sn$ calcd.: C, 48.40; H, 8.12%.

1-Phenyl-1-trimethylstannylethene[9]

B.p. 103°C (bath temp., 6 Torr); IR (neat) 2930, 1590, 1480, 1440, 1020, 870 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.25 (s, 9H), 5.48 (d, J 2.3 Hz, 1H), 6.08 (d, J 2.3 Hz, 1H), 7.0–7.4 (m, 5H).

(E)-1-Trimethylstannyl-1-octene [9,22]

Treatment of (E)-1-iodo-1-octene with $Me_3SnMgMe$ and CuCN as described above provided the title vinylstannane. A 63% yield was determined by GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 110°C) using hexadecane as the internal standard: b.p. 75°C (bath temp., 8 Torr); IR (neat): 2870, 1460, 1180, 990 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.06 (s, 9H), 0.93 (t, J 6 Hz, 3H), 1.31 (bs, 8H), 2.00–2.19 (m, 2H), 5.90–6.00 (m, 2H).

(Z)-1-Trimethylstannyl-1-octene [9,22]

Treatment of (Z)-1-octene with $Me_3SnMgMe$ and CuCN gave the title compound in addition to the (E)-isomer. The Z/E ratio was determined from the ^{119}Sn NMR spectrum. A 72% yield was determined by GLPC (Silicone OV 17 3% on Uniport HP, 2 m, 110°C) using hexadecane as the internal standard: b.p. 78°C (bath temp., 8 Torr); IR (neat): 2870, 1590, 1450, 1180, 880 cm^{-1}; ^1H NMR ($CDCl_3$): 0.12 (s, 9H), 0.93 (t, J 6Hz, 3H), 1.31 (bs, 8H), 2.00–2.19 (m, 2H), 5.80 (d, J 10.1 Hz, 1H), 6.47 (dd, J 10.1, 7.2 Hz, 1H).

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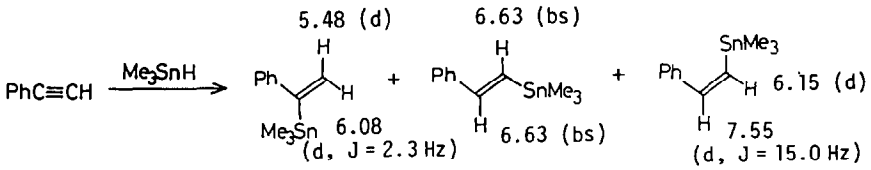

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