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Et_3B INDUCED RADICAL ADDITION OF Ph_3SnH TO ACETYLENES AND ITS APPLICATION TO CYCLIZATION REACTION

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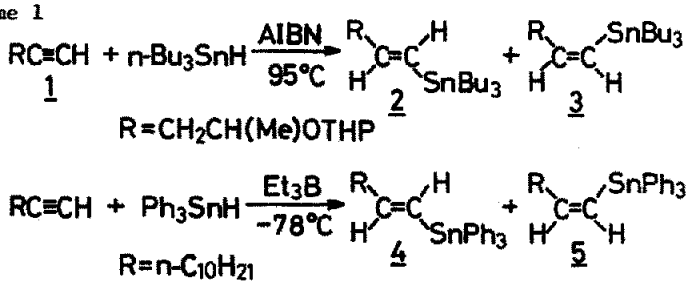
Abstract: An addition of a catalytic amount of Et_3B to a solution of acetylenic compound and Ph_3SnH in toluene promotes the formation of alkenylstannanes effectively. Triphenylstannyl group adds to terminal acetylenic carbon regioselectively to give a mixture of (E)- and (Z)-1-triphenylstannyl-1-alkenes. The E/Z ratios of double bonds are generally 8/2-7/3. The reaction is successfully applied to the radical cyclization reaction.

Free radical reactions have been used increasingly in recent years for the synthesis of organic molecules.[1] Only little attention, however, has been payed to the methods for the primary generation of radicals. Photoinitiation and chemical initiation are general two methods and initiators such as dialkylperoxides and azobisisobutyronitrile (AIBN) are widely and exclusively used in the latter case. Here we report that trialkylborane is an effective radical initiator and mediates a facile addition of R_3SnH to an acetylenic bond to give vinylstannane regioselectively.

The reaction producing alkenyltrialkylstannanes is of particular synthetic interest, since the alkenyl group of such products can be selectively transfered from tin to various other atoms including C, H, halogen, and Li.[2] The hydrostannation of acetylenes is the simplest and most direct route to alkenylstannanes.[3,4] For instance, heating acetylene, tetrahydropyranyl ether of 4-pentyn-2-ol (1) for 3 h at 95 °C with n-Bu_3SnH in the presence of a catalytic amount of AIBN has been reported to give alkenylstannanes 2, 3 in a ratio of 85/15 (Scheme 1).[5] Meanwhile, we have found that an addition of a catalytic amount of Et_3B to a solution of acetylenic compound and Ph_3SnH in toluene facilitates the formation of alkenylstannanes effectively.[6] The reaction proceeded

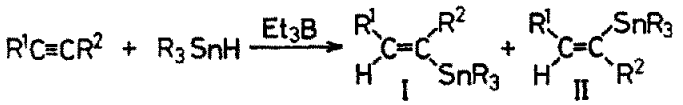
Scheme 1



easily at low temperature such as -78 °C. The reactions were mostly, however, performed at room temperature because of the convenience of the operation (see Table 1).

Typical procedure is as follows. A hexane solution of Et_3B[7] (1.0 M, 0.1 ml, 0.1 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and triphenyltin hydride (0.42 g, 1.2 mmol) in toluene (8.0 ml) at 25 °C under an argon atmosphere. After stirring for 20 min at 25 °C, the reaction mixture was poured into water. Extractive workup followed by purification gave alkenylstannanes **4**, **5** as a stereoisomeric mixture (0.41 g, 80% yield, **4**/**5** = 79/21). The representative results are summarized in Table 1. Triphenylstannyl group adds to terminal acetylenic carbon regioselectively but nonstereoselectively to give a mixture of (E)- and (Z)-1-triphenylstannyl-1-alkenes. The E/Z ratios of double bonds were generally 8/2-7/3 and not affected by solvents. The ratios of (E)-1-triphenylstannyl-1-dodecene (**4**) and (Z) isomer (**5**) were 79/21, 80/20, 77/23, and 63/37 in toluene, benzene, Et_2O, and THF, respectively. The ratios of E to Z products were also quite insensitive to reaction temperature between -78 °C and 80 °C.[8] In contrast, the E/Z ratios depend on the reaction temperature in the case of uncatalyzed hydrostannation.[5] Heating a mixture of 1-dodecyne and Ph_3SnH at 80 °C for 1.5 h gave a mixture of (E)- and (Z)-1-triphenylstannyl-1-dodecene (**4**/**5** = 22/78) in 53% combined yield. A mixture of (E) and (Z) isomer (**4**/**5** = 75/25, 65% yield) was obtained after 5 h at 150 °C. Phenylacetylene and trimethylsilylacetylene provided (E) vinylstannanes exclusively. An addition of n-Bu_3SnH took longer reaction time and gave the corresponding vinylstannanes in poor yields. For example, the reaction of 1-dodecyne with n-Bu_3SnH in the presence of Et_3B provided 1-tributylstannyl-1-dodecene in only 40% yield after stirring for 2 h

Table 1. Triethylborane induced hydrostannation of acetylenes[a]

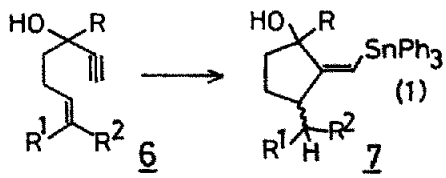


Entry	Substrate R^1	Substrate R^2	Reagent	Reaction Time(h)	Y(%)	Product ratio of I:II
1	n-$C_{10}H_{21}$	H	Ph_3SnH	0.3	80	79:21
2			n-Bu_3SnH	2.0	40	80:20
3	$PhCH_2OCH_2CH_2$	H	Ph_3SnH	0.3	79	69:31
4			n-Bu_3SnH	10	71	90:10
5	$THPOCH_2CH_2$	H	Ph_3SnH	0.3	81	80:20
6	$HOCH_2CH_2$	H	Ph_3SnH	0.3	87	82:18
7	Ph	H	Ph_3SnH	0.3	75	100:0
8	Me_3Si	H	Ph_3SnH	0.3	83[b]	100:0
9	n-C_5H_{11}	n-C_5H_{11}	Ph_3SnH	10	86[c]	0:100
10	Ph	Me	Ph_3SnH	1.0	74	25:75

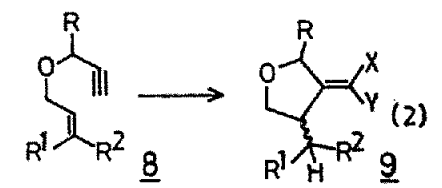
a) Acetylene (1.0 mmol), R_3SnH (1.2 mmol), and Et_3B (0.1 mmol) were employed. The reactions were performed at room temperature. b) Excess of trimethylsilylacetylene (5.0 mmol) and Ph_3SnH (1.0 mmol) were employed and the yield was based on Ph_3SnH. c) Excess of Ph_3SnH (5.0 mmol) was used.

at room temperature (Entry 2 in Table 1). Heating of a reaction mixture was essential for having a successful yield. A mixture of 1-octyne (45 mmol), n-Bu_3SnH (38 mmol), and Et_3B (1.0 M hexane solution, 15 ml, 15 mmol) was heated at 70 °C for 7 h to give 1-tributylstannyl-1-octene as a stereoisomeric mixture (E/Z = 3/1, 32 mmol) in 83% yield.[9]

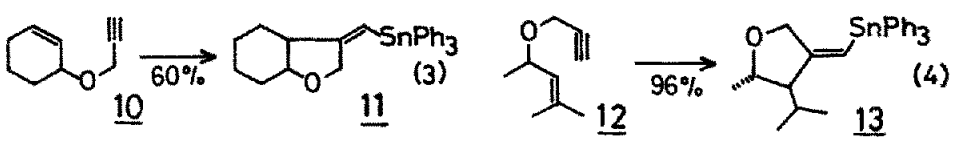
The Et_3B-induced reaction has two characteristics: (1) The triphenyltin radical can be generated at low temperature such as -78 °C and thereby the hydrostannation of acetylenes proceeds at such low temperature, and (2) the reaction takes place easily in various solvents under high diluted conditions in contrast to the previously reported hydrostannation reaction which proceeds by heating a mixture of acetylene and trialkylstannane without solvent. Taking advantage of second characteristic, we applied our new method to the radical cyclization reaction shown in eq (1)-(4).[10,11] The concentration of Ph_3SnH affected the yield and distribution of the products. Uncyclized product was obtained in addition to the cyclized desired compound in a higher concentration. For instance, the compound **6a** gave cyclized product **7a** exclusively at 0.012 M concentration of Ph_3SnH, while, at 0.30 M concentration, **7a** and uncyclized product, $Me_2C{=}CHCH_2CH_2C(OH)MeCH{=}CHSnPh_3$ were obtained in 60% and 15% yield, respectively. Heating a mixture of **6a** and Ph_3SnH without solvent at 80 °C for 15 h gave a complex mixture consisting of (E)- and (Z)-vinylstannanes ($Me_2C{=}CH$-$CH_2CH_2C(OH)MeCH{=}CHSnPh_3$, 46%), regioisomer ($Me_2C{=}CHCH_2CH_2C(OH)MeC(SnPh_3){=}CH_2$, 9%), and the desired cyclized product 7a (38% yield).



a: R = Me R^1= R^2= Me 75% (78/22)
b: R = Me R^1= R^2= H 50% (80/20)
c: R = Me R^1= Me R^2= $CH_2CH_2CH{=}CMe_2$ 78% (79/21)
d: R = n-C_5H_{11} R^1= H R^2= Ph 87% (63/37)

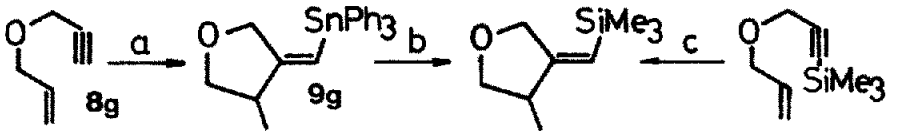


a: R = H R^1= R^2= Me X = $SnPh_3$ Y = H (78%)
b: R = H R^1= H R^2= n-C_3H_7 X = $SnPh_3$ Y = H (85%)
c: R = n-Bu R^1= R^2= Me X = $SnPh_3$ Y = H (69%, 64/36)
d: R = H R^1= R^2= Me X = Ha Y = Hb
e: R = H R^1= R^2= Me X = $SnPh_3$ Y = D
f: R = H R^1= R^2= Me X = H Y = D



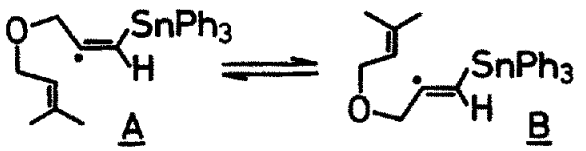
It is worth noting that the serious limitation, nonstereoselectivity shown in Table 1 was overcome in these cyclization reactions and the cyclized products consist of only (Z) isomer without contamination by the other stereoisomer. The compound **9a**, **9b**, **11**, and **13** showed one signal each for olefinic protons on ^1H NMR spectra and also on ^{119}Sn NMR. The compound **9d** derived from **9a** by destannylation (n-BuLi/THF, H_2O)[12] showed ^1H NMR signals at δ 5.00 (m, Ha) and 4.95 (m, Hb). Treatment of the deuterated acetylene **8a** ($DC{\equiv}CCH_2OCH_2CH{=}CMe_2$) with Ph_3SnH followed by destannylation provided **9f** whose ^1H NMR spectrum showed

only one signal in the olefinic region at δ 4.99. The complete disappearance of the higher field signal is consistent with a formation of single stereoisomer **9e**. The structure of the cyclized product was also confirmed as follows. Treatment of **8g** (R = R^1 = R^2 = H) with our new system provided **9g** (32% yield) along with six-membered ring product, 3-(triphenylstannyl)methylenetetrahydropyran (45%).[13] The vinylstannane **9g** was converted into vinylsilane by treatment with n-BuLi and Me_3SiCl, which was identical with the sample prepared from allyl (trimethylsilyl)propargyl ether following Negishi's procedure.[14]

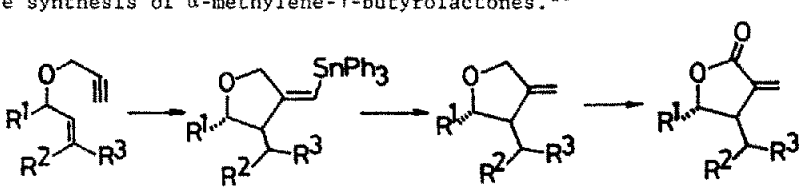


a: Ph_3SnH, BEt_3 b: BuLi/Me_3SiCl c: $ZrCp_2$

The formation of a single isomer may be explained by assuming the equilibrium between **A** and **B**. The intermediate **A** cyclized more readily than **B**. Alternatively, trans addition product **A**, produced under kinetic conditions, may immediately attack the properly located double bond before being converted into equilibrium mixture (**A** and **B**).



The compounds **6a-d**, **8c** provided cis-trans stereoisomeric mixtures concerning the substituents on a five-membered ring. In contrast, the compound **10** gave cis isomer **11** and the compound **12** afforded trans isomer **13**, respectively as a single product.[15] These reactions were successfully applied to the stereoselective synthesis of α-methylene-γ-butyrolactones.[16]

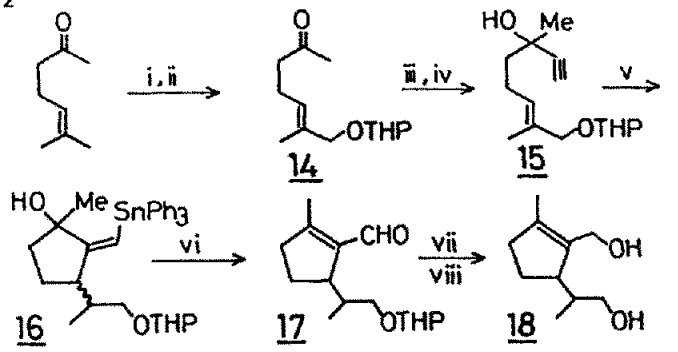


Scheme 2 illustrates the synthesis of dehydroiridodiol and isodehydroiridodiol. Triethylborane induced triphenyltin radical addition-cyclization process provided vinylstannane **16** (84%) starting from readily available propargylic alcohol **15**. Collins oxidation of **16** gave **17** (54%). Diisobutylaluminum hydride reduction followed by treatment with p-TsOH provided a mixture of dehydroiridodiol (3R^*, 8S^*) and isodehydroiridodiol (3R^*, 8R^*) (26/74, 58% overall yield from **17**)[17] which was easily separated by preparative tlc on silica gel.

The reaction was not so effective for the formation of six-membered ring. For instance, treatment of (Z)-$HC{\equiv}CCH_2OCH_2CH_2CH{=}CHEt$ gave the desired cyclized product in only 28% yield along with uncyclized vinylstannane (49%).

Next, we examined the reaction mechanism as well as the role of Et_3B. An addition of galvinoxyl, an efficient scavenger of free radicals,[18] to a reaction mixture of 1-dodecyne, Ph_3SnH, and Et_3B resulted in a recovery of the acetylene.

Scheme 2



i) SeO_2/EtOH-H_2O ii) Dihydropyran, TsOH iii) $Me_3SiC{\equiv}CLi$ iv) KF/DMSO v) Ph_3SnH, Et_3B vi) $CrO_3{\cdot}2Py$ vii) $^iBu_2AlH$ viii) TsOH/MeOH

Consequently, the addition reaction must involve a free radical chain mechanism. The organoboranes have been reported to be excellent sources of free radicals in the presence of oxygen.[19] Indeed, we have confirmed that (1) the hydrostannation reaction was very sluggish under strictly inert argon atmosphere and (2) oxygen initiates the Et_3B-mediated radical addition of Ph_3SnH to acetylene. Controlled experiment[20] was carried out as follows using general Schlenk technique. To an NMR tube benzene-$\underline{d}_6$ was introduced under argon atmosphere. 1-Dodecyne and Ph_3SnH were added, followed by Et_3B. The reaction was monitored by ^{1}H-NMR every 15 min. Only small amount of 1-triphenylstannyl-1-dodecene (<10%) was detected even after 3.5 h. Then, oxygen was introduced by syringe and the yield of vinylstannane immediately increased (See experimental part).

EXPERIMENTAL

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by an air bath temperature without correction. All melting points were obtained on Yanaco MP-50929 melting points apparatus and are uncorrected. The IR spectra were determined on a JASCO IR-810 spectrometer, the mass spectra on a Hitachi M-80 machine, the proton NMR spectra on Varian EM-390 and Varian XL-200 spectrometers, and the ^{119}Sn NMR spectra on a JEOL JNM-FX 90Q spectrometer. The chemical shifts of the proton NMR are given in δ with Me_4Si as an internal standard, and those of the ^{119}Sn NMR are given in δ with Me_4Sn as an internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Purification of products was performed by column chromatography on silica gel or preparative thin-layer chromatography (TLC).

General Procedure for Triethylborane-induced Hydrostannation of Acetylenes. Hydrostannation of 1-dodecyne is representative. A hexane solution of Et_3B (1.0 M, 0.1 ml, 0.1 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and triphenyltin hydride (0.42 g, 1.2 mmol) in toluene (5.0 ml) at 25 °C under an argon atmosphere. After stirring for 20 min at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was submitted to preparative tlc on silica gel to give (E)- and (Z)-1-triphenylstannyl-1-dodecene as a stereoisomeric mixture (0.41g, 80% yield, 4/5 = 79/21) which was identical with authentic samples.[21]

4-Benzyloxy-1-triphenylstannyl-1-butene,[21] 4-Benzyloxy-1-tributylstannyl-1-butene,[4d] 1-Phenyl-2-(triphenylstannyl)ethene,[21] and 1-Trimethylsilyl-2-(triphenylstannyl)ethene.[22] The physical data of these compounds are shown in the literature.

Tetrahydropyranyl Ether of 4-Triphenylstannyl-3-buten-1-ol: bp 170 °C (bath temp, 0.3 Torr); IR (neat) 3060, 3044, 2940, 2866, 1429, 1119, 1075, 1032, 727, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) (E-isomer) δ 1.45-1.95 (m, 6H), 2.65 (dt, J = 5.0, 7.0 Hz, 2H), 3.46-4.02 (m, 4H), 4.65-4.75 (m, 1H), 6.35-6.47 (m, 2H), 7.40-7.90 (m, 15H), (Z-isomer) δ 1.45-1.95 (m, 6H), 2.50 (dt, J = 7.5, 8.0 Hz, 2H), 3.30-4.02 (m, 4H), 4.46-4.53 (m, 1H), 6.25 (d, J = 12.2 Hz, 1H), 6.98 (dt, J = 12.2, 7.5 Hz, 1H), 7.40-7.90 (m, 15H); ^{119}Sn-NMR δ -137.0 (E), -150.9 (Z). Found: C, 64.14; H, 6.05%. Calcd for $C_{24}H_{30}O_2Sn$: C, 64.19; H, 5.98%.

4-Triphenylstannyl-3-buten-1-ol: mp 85 °C (hexane); IR (KBr) 3312, 3058, 3012, 2984, 2924, 1600, 1480, 1428, 1333, 1303, 1022, 997, 726, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) (E-isomer) δ 1.60 (s, 1H), 2.58 (dt, J = 6.0, 5.8 Hz, 2H), 3.78 (t, J = 5.8 Hz, 2H), 6.25 (dt, J = 18.0, 6.0 Hz, 1H), 6.44 (d, J = 18.0 Hz, 1H), 7.35-7.83 (m, 15H); (Z-isomer) δ 1.45 (s, 1H), 2.39 (dt, J = 7.2, 6.0 Hz, 2H), 3.57 (t, J = 6.0 Hz, 2H), 6.13 (d, J = 12.0 Hz, 1H), 6.88 (dt, J = 12.0, 7.2 Hz, 1H), 7.35-7.83 (m, 15H); ^{119}Sn-NMR δ -137.5 (E), -151.3 (Z). Found: C, 62.46; H, 5.13%. Calcd for $C_{22}H_{22}OSn$: C, 62.75; H, 5.27%.

(Z)-6-Triphenylstannyl-6-dodecene: bp 170 °C (bath temp, 0.3 Torr); IR (neat) 3060, 2952, 2922, 2852, 1465, 1458, 1428, 1074, 908, 725, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.70-0.83 (m, 6H), 0.85-1.54 (m, 12H), 2.03 (dt, J = 7.1, 7.1 Hz, 2H), 2.30 (t, J = 7.0 Hz, 2H), 6.33 (t, J = 7.1 Hz, 1H), 7.35-7.80 (m, 15H); ^{119}Sn-NMR δ -139.4. Found: C, 69.66; H, 7.51%. Calcd for $C_{30}H_{38}Sn$: C, 69.65; H, 7.40%.

1-Phenyl-2-triphenylstannyl-1-propene: mp 153.2 °C (hexane); IR (KBr) 3058, 3014, 2938, 1479, 1428, 1074, 727, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) (E-isomer) δ 2.31 (d, J = 1.9 Hz, 3H), 6.95 (q, J = 1.9 Hz, 1H), 7.15-7.85 (m, 20H); (Z-isomer) δ 2.23 (d, J = 1.8 Hz, 3H), 6.98 (q, J = 1.8Hz, 1H), 7.15-7.85 (m, 20H); ^{119}Sn-NMR δ -139.0 (E), -123.1 (Z). Found: C, 69.28; H, 5.03%. Calcd for $C_{27}H_{24}Sn$: C, 69.42; H, 5.18%.

3,7-Dimethyl-6-octen-1-yn-3-ol (**6a**): bp 94 °C (bath temp, 20 Torr); IR (neat) 3360, 3302, 2968, 2926, 2856, 1451, 1376, 1157, 1121, 1085, 907 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.50 (s, 3H), 1.60-1.76 (m, 2H), 1.66 (s, 3H), 1.70 (s, 3H), 2.10-2.43 (m, 3H), 2.47 (s, 1H), 5.12-5.25 (m, 1H). Found: m/e 152.1222. Calcd for $C_{10}H_{16}O$: M, 152.1201.

3-Methyl-6-hepten-1-yn-3-ol (**6b**): bp 83.5 °C (bath temp, 1.0 Torr); IR (neat) 3366, 3302, 2976, 2930, 1641, 1450, 1374, 1149, 1118, 911, 630 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.52 (s, 3H), 1.72-1.85 (m, 2H), 2.25-2.42 (m, 3H), 2.47(s, 1H), 5.01 (br.d, J = 10.2 Hz, 1H), 5.10 (br.d, J = 17.1 Hz, 1H), 5.89 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H).

3-Pentyl-7-phenyl-6-hepten-1-yn-3-ol (**6d**): IR (neat) 3420, 3302, 2930, 2862, 1453, 1379, 1071, 1025, 733, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.75-2.60 (m, 15H), 3.35-3.70 (m, 2H), 6.27 (dt, J = 15.5, 6.5 Hz, 1H), 6.46 (d, J = 15.5 Hz, 1H), 7.15-7.70 (m, 5H).

3-Methyl-2-butenyl 2-Propynyl Ether (**8a**): bp 101 °C (bath temp, 760 Torr); IR (neat) 3294, 2970, 2914, 2854, 1443, 1378, 1355, 1076, 1025 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.70 (s, 3H), 1.76 (s, 3H), 2.43 (bs, 1H), 4.07 (d, J = 7.2 Hz, 2H), 4.13 (bs, 2H), 5.38 (t, J = 7.2 Hz, 1H). Found: m/e 124.0918. Calcd for $C_8H_{12}O$: M, 124.0608.

2-Hexenyl 2-Propynyl Ether (**8b**): bp 88 °C (bath temp, 20 torr); IR (neat) 3300, 2956, 2926, 2858, 1458, 1440, 1356, 1103, 1079, 1028, 971 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3H), 1.33-1.55 (m, 2H), 1.99-2.09 (m, 2H), 2.42 (t, J = 2.4 Hz, 1H), 4.02 (dd, J = 6.2, 1.0 Hz, 2H), 4.13 (d, J = 2.4 Hz, 2H), 5.47-5.66 (m, 1H), 5.67-5.85 (m, 1H). Found: C, 77.93; H, 10.33%. Calcd for $C_9H_{14}O$; C, 78.21; H, 10.21%.

3-Methyl-2-butenyl 1-Butyl-2-propynyl Ether (**8c**): bp 97 °C (bath temp, 20 Torr); IR (neat) 3304, 2954, 2928, 2860, 1458, 1449, 1378, 1336, 1117, 1076, 1029, 985, 653, 624 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.20-1.55 (m, 6H), 1.71 (s, 3H), 1.75 (s, 3H), 2.42 (d, J = 2.1 Hz, 1H), 3.94-4.33 (m, 3H), 5.31-5.45 (m, 1H). Found: C, 79.57; H, 11.18%. Calcd for $C_{12}H_{20}O$; C, 79.94; H, 11.18%.

2-Cyclohexenyl 2-Propynyl Ether (**10**) and 1, 3-Dimethyl-2-butenyl 2-Propynyl Ether (**12**). The data of these compounds are described in Ref. 16.

General Procedure for Radical Cyclization of Enynes. Transformation of 3,7-dimethyl-6-octen-1-yn-3-ol (**6a**) into 3-isopropyl-1-methyl-2-triphenylstannylmethylene-1-cyclopentanol (**7a**) is representative. A hexane solution of Et_3B (1.0 M, 0.2 ml, 0.2 mmol) was added to a solution of Ph_3SnH (0.42 g, 1.2 mmol) and the acetylene (**6a**) (0.15 g, 1.0 mmol) in toluene (100 ml) at 25 °C under an argon atmosphere. After stirring for 3 h at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. Purification by preparative tlc on silica gel gave the cyclized product (**7a**) (0.37 g, 75% yield) as a stereoisomeric mixture (78/22): IR (neat) 3566, 3058, 2954, 1428, 1195, 1073, 727, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.84 (d, J = 6.5 Hz, 3H), 0.96 (s, 3H), 1.00 (d, J = 6.5 Hz, 3H), 1.2-2.1 (m, 6H), 2.64 (m, 1H), 6.03 (d, J = 2.2 Hz, for minor compound, 0.22H), 6.10 (d, J = 2.2 Hz, for major compound, 0.78H), 7.25-7.80 (m, 15H); ^{119}Sn-NMR δ -147.8 (minor), -150.2 (major). Found: C, 66.71; H, 6.34%. Calcd for $C_{28}H_{32}OSn$: C, 66.83; H, 6.41%.

1,3-Dimethyl-2-triphenylstannylmethylene-1-cyclopentanol (**7b**). An 80/20 mixture of diastereomers was obtained. The physical data for major isomer are as follows: mp 138 °C (hexane); IR (neat) 3546, 3430, 3046, 2956, 2864, 1618, 1426, 1190, 1073, 726, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.20 (d, J = 7.0 Hz, 3H), 1.05-2.10 (m, 5H), 2.63-2.88 (m, 1H), 6.10 (d, J = 2.2 Hz, 1H), 7.30-7.85 (m, 15H); ^{119}Sn-NMR δ -152.4. Found: C, 65.57; H, 5.93%. Calcd for $C_{26}H_{28}OSn$; C, 65.72; H, 5.94%.

1-Methyl-2-triphenystannylmethylene-1-cyclohexanol. Radical cyclization reaction of **7b** produced the corresponding five-membered ring compound, **8b** in 50% yield along with the title six-membered ring product[13] in 31% yield: mp 113 °C (hexane); IR (KBr) 3560, 3058, 2930, 1427, 1074, 727, 699 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.27 (s, 3H), 1.00-1.95 (m, 7H), 2.27-2.65 (m, 2H), 5.82 (d, J = 1.2 Hz, 1H), 7.25-7.83 (m, 15H); ^{119}Sn-NMR δ -161.7. Found: C, 65.69; H, 5.90%. Calcd for $C_{26}H_{28}OSn$: C, 65.72; H, 5.94%.

3-Benzyl-1-pentyl-2-triphenylstannylmethylene-1-cyclopentanol (**7d**, 63/37 mixture of diastereomers): mp 110 °C (hexane); IR (neat) 3560, 2952, 2926, 2852, 1427, 1073, 726, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.70-2.11 (m, 16H), 2.50-2.77 (m, 1H), 2.80-3.31 (m, 2H), 6.17 (d, J = 1.6 Hz, 0.63H), 6.21 (d, J = 2.0 Hz, 0.37H), 7.20-7.85 (m, 20H); ^{119}Sn-NMR δ -153.2 (major). A signal for minor isomer could not be detected. Found: C, 71.06; H, 6.69%. Calcd for $C_{36}H_{40}OSn$: C, 70.85; H, 6.45%.

(Z)-4-Isopropyl-3-(triphenylstannylmethylene)oxolane (**9a**): bp 165 °C (bath temp, 0.2 Torr); IR (neat) 3012, 2922, 1429, 1074, 726, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.96 (d, J = 6.5 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H), 2.05 (m, 1H), 2.73 (m, 1H) 3.82 (dd, J = 5.5, 9.0 Hz, 1H), 3.95 (dd, J = 7.5, 9.0 Hz, 1H), 4.08 (brs, 2H), 6.12 (m, 1H) 7.3-7.8 (m, 15H); ^{119}Sn-NMR ($CDCl_3$) δ -142.9. Found: C, 65.55; H,

5.82%. Calcd for $C_{26}H_{28}OSn$: C, 65.72; H, 5.94%.

(Z)-4-Butyl-3-(triphenylstannylmethylene)oxolane (**9b**): bp 160 °C (bath temp, 0.2 Torr); IR (neat) 3060, 2952, 2922, 2852, 1480, 1459, 1429, 1074, 726, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.92 (t, J = 6.3 Hz, 3H), 1.02-0.85 (m, 6H), 2.63-2.78 (m, 1H), 3.37-4.20 (m, 4H), 6.07 (bs, 1H), 7.25-7.70 (m, 15H); ^{119}Sn-NMR δ -145.6. Found: C, 66.06; H, 6.18%. Calcd for $C_{25}H_{30}OSn$: C, 66.29; H, 6.18%.

(Z)-2-Butyl-4-isopropyl-3-(triphenylstannylmethylene)oxolane (**9c**, 64/36 mixture of diastereomers: 180 °C (bath temp, 1.0 Torr); IR (neat) 3080, 2928, 2883, 1429, 1074, 736, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.65 (t, J = 6.9Hz, 3H), 0.80-1.48 (m, 6H), 0.92 (for major product, d, J = 6.7 Hz, 1.92H), 0.97 (for minor product, d, J = 6.5 Hz, 1.08H), 1.22 (major, d, J = 6.7 Hz, 1.92H), 1.40 (minor, d, J = 6.8 Hz, 1.08H), 1.88-2.17 (m, 1H), 2.55-2.85 (m, 1H), 3.65-4.20 (m, 3H), 6.3 (bs, 1H), 7.35-7.80 (m, 15H); ^{119}Sn-NMR δ -146.4 (major), -146.2 (minor). Found: C, 67.66; H,6.94%. Calcd for $C_{30}H_{36}OSn$: C, 67.82; H, 6.83%.

(Z)-cis-Hexahydro-3-(triphenylstannylmethylene)benzofran (**11**) and (Z)-trans-3-Isopropyl-2-methyl-4-(triphenylstannylmethylene)oxolane (**13**). The physical data for these compounds are given in Ref. 16.

(Z)-4-Methyl-3-(triphenylstannylmethylene)oxolane (**9g**): ^{1}H-NMR ($CDCl_3$) δ 1.19 (d, J = 6.8 Hz, 3H), 2.73-2.95 (m, 1H), 4.00-4.25 (m, 4H), 6.06 (bs, 1H), 7.33-7.80 (m, 15H).

(Z)-4-Methyl-3-(trimethylsilylmethylene)oxolane: ^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.08 (d, J = 7.0 Hz, 3H), 2.55-2.76 (m, 1H), 4.02-4.48 (m, 4H), 5.39 (bs, 1H).

3-(Triphenylstannylmethylene)tetrahydropyran. Radical cyclization reaction of **8g** gave **9g** (32% yield) along with six-membered ring product as an isomeric mixture (E/Z = 1/1). faster moving band (Rf = 0.5, hexane/ethyl acetate = 20/1): ^{1}H-NMR ($CDCl_3$) δ 1.75-1.89 (m, 2H), 2.50-2.62 (m, 2H), 3.36 (d, J = 8.5 Hz, 1H), 3.40 (d, J = 8.4 Hz, 1H), 4.04 (s, 2H), 5.87 (s, 1H), 7.33-7.80 (m, 15H). slower moving band (Rf = 0.4): mp 112.7 °C (methanol) IR (KBr) 3060, 3020, 2922, 2840, 1427, 1082, 1073, 727, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.57-1.73 (m, 2H), 2.36 (t, J = 5.5 Hz, 2H), 3.72 (t, J = 5.2 Hz, 2H), 4.20 (s, 2H), 5.92 (s, 1H), 7.32-7.80 (m, 15H). Found: C, 64.64; H, 5.60%. Calcd for $C_{24}H_{24}OSn$: C, 64.47; H, 5.41%.

(E)-7-Hydroxy-6-methyl-5-hepten-2-one: IR (neat) 3376, 2916, 2856, 1707, 1655, 1407, 1363, 1222, 1161, 1012 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.68 (s, 3H), 2.15 (s, 3H), 2.26-2.44 (m, 2H), 2.49-2.60 (m, 2H), 4.00 (s, 3H), 5.37 (t, J = 7.1 Hz, 1H).

Tetrahydropyranyl Ether of (E)-7-Hydroxy-6-methyl-5-hepten-2-one (**14**): IR (neat) 2938, 2864, 1717, 1440, 1356, 1158, 1135, 1119, 1077, 1022, 977, 905, 869 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.37-1.93 (m, 6H), 1.63 (s, 3H), 2.10 (s, 3H), 2.21-2.38 (m, 2H), 2.41-2.55 (m, 2H), 3.40-3.57 (m, 1H), 3.75-4.15 (m, 3H), 4.52-4.62 (m, 1H), 5.35 (t, J = 7.0 Hz, 1H).

3,7-Dimethyl-8-tetrahydropyranyloxy-6-octene-1-yn-3-ol (**15**): bp 126 °C (bath temp, 1.0 Torr); IR (neat) 3416, 3302, 2936, 2866, 1454, 1442, 1385, 1357, 1201, 1184, 1157, 1118, 1076, 1053, 1021, 978, 905, 867 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.51 (s, 3H), 1.68 (s, 3H), 1.50-2.00 (m, 9H), 2.15-2.44 (m, 2H), 2.45 (s, 1H), 3.47-3.60 (m, 1H), 3.86 (d, J = 11.5 Hz, 1H), 3.78-3.96 (m, 1H), 4.11 (d, J = 11.5 Hz, 1H), 4.58-4.68 (m, 1H), 5.50 (t, J = 7.0 Hz, 1H). Found: C, 71.10; H, 9.67%. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59%.

1-Methyl-3-(1-methyl-2-tetrahydropyranyloxy)ethyl-2-triphenylstannylmethylene-1-cyclopentanol (**16**, mixture of 8 diastereomers): ^{1}H-NMR ($CDCl_3$) δ

0.80-1.20 (m, 3H), 1.25-2.43 (m, 15H), 2.65-2.85 (m, 1H), 2.90-3.95 (m, 4H), 4.50-4.64 (m, 1H), 6.15 (bs, 1H), 7.30-7.80 (m, 15H); ^{119}Sn-NMR (for major 2 isomers) δ -149.5, -151.4. Found: C, 65.64; H, 6.81%. Calcd for $C_{33}H_{40}O_3Sn$: C, 65.69; H, 6.68%.

2-Methyl-5-(1-methyl-2-tetrahydropyranyloxy)ethylcyclopentene-1-carboaldehyde (17, mixture of 4 diastereomers, (a):(b):(c):(d) = 32:34:16:18): bp 108 °C (bath temp, 1.0 Torr); IR (neat) 2938, 2868, 665, 1440, 1379, 1440, 1379, 1350, 1260, 1200, 1120, 1077, 1061, 1031, 976, 904 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.67 (for (d), d, J = 7.0 Hz, 0.54H), 0.72 (for (c), d, J = 6.9 Hz, 0.48H), 0.95 (for (b), d, J = 7.0 Hz, 1.02H), 0.96 (for (a), d, J = 7.0 Hz, 0.96H), 1.40-2.05 (m, 9H), 2.13 (s, 3H), 2.24-2.70 (m, 3H), 3.01-3.95 (m, 4H), 4.48-4.67 (m, 1H), 10.0 (s, 1H). Found: C, 71.49; H, 9.50%. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59%.

Dehydroiridodiol (3R*,8S*): ^{1}H-NMR ($CDCl_3$) δ 0.88 (d, J = 7.0 Hz, 3H), 1.51-2.47 (m, 6H), 1.71 (s, 3H), 2.80 (bs, 1H), 3.46 (dd, J = 6.0, 11.0 Hz, 1H), 3.56 (dd, J = 8.0, 11.0 Hz, 1H), 4.21 (s, 1H).

Isodehydroiridodiol (3R*,8R*): ^{1}H-NMR ($CDCl_3$) δ 0.72 (d, J = 6.9 Hz, 3H), 1.52-2.20 (m, 5H), 1.72 (bs, 3H), 2.25-2.40 (m, 2H), 3.20 (bs, 1H), 3.51 (dd, J = 7.2, 10.2 Hz, 1H), 3.56 (dd, J = 7.2, 10.5 Hz, 1H), 4.06 (d, J = 12.3 Hz, 1H), 4.30 (d, J = 12.3 Hz, 1H).

(Z)-3-Hexenyl Propargyl Ether: IR (neat) 3290, 2962, 2872, 1458, 1357, 1095, 1024, 973, 665 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H), 1.98-2.15 (m, 2H), 2.30-2.48 (m, 2H), 2.43 (t, J = 2.3 Hz, 1H), 3.54 (t, J = 7.0 Hz, 2H), 4.16 (d, J = 2.3 Hz, 2H), 5.27-5.60 (m, 2H).

3-Propyl-2-(triphenylstannylmethylene)tetrahydropyran: IR (neat) 3044, 2926, 1609, 1480, 1428, 1075, 726, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.96 (t, J = 7.0 Hz, 3H), 1.20-2.12 (m, 6H), 2.35-2.54 (m, 1H), 3.58-3.74 (m, 1H), 3.85-4.01 (m, 1H), 3.93 (d, J = 13.0 Hz, 1H), 4.18 (d, J = 13.0 Hz, 1H), 5.90 (bs, 1H), 7.33-7.77 (m, 15H); ^{119}Sn-NMR δ -144.0.

Reaction of 1-Dodecyne, Ph_3SnH, and Et_3B in the Presence of Galvinoxyl. Galvinoxyl (4.2 mg, 0.01 mmol) was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and Ph_3SnH (0.39 g, 1.1 mmol) in toluene (8 ml) at 25 °C under an argon atmosphere. A hexane solution of Et_3B (1.0 M, 0.1 ml, 0.1 mmol) was added to the resulting yellow solution and the whole was stirred for 3 h at 25 °C. Workup followed by purification by preparative tlc on silica gel afforded 1-dodecyne (0.14 g, 84% recovery). 1-Triphenylstannyl-1-dodecene was not detected in the reaction mixture.

Monitoring the Et_3B-Induced Reaction of 1-Dodecyne with Ph_3SnH by ^{1}H-NMR (Controlled Experiment). The experiment was carried out using general Schlenk technique. 1-Dodecyne, Ph_3SnH, and Et_3B were freshly distilled under argon atmosphere. Benzene-d_6 (freshly distilled from Na-K alloy, 0.5 ml) was introduced into an NMR tube under argon atmosphere. 1-Dodecyne (21 μl, 0.10 mmol) and Ph_3SnH (28 μl, 0.11 mmol) were added. Then, Et_3B (5 μl, 0.04 mmol) was added and the NMR tube was closed by a rubber serum cap and sealed by parafilm. The reaction was monitored by ^{1}H-NMR every 15 min. NMR analysis immediately after addition of Et_3B showed that any trace of 1-triphenylstannyl-1-dodecene was not produced. Small amount of the product (<10%) was detected after 30 min, but the yield did not increase for next 2.5 h. After 3.5 h, oxygen (60 μl, 2.7 mol) was introduced by syringe. The reaction immediately took place and the yield of vinylstannane jumped up to 50% after 1 h and then stayed between 50% and 55%. An addition of another oxygen (60 μl, 2.7 mol) raised the yield of the product to 70%.

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