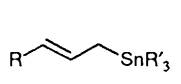
Synthesis of α-Substituted Allyl- and Homoallyl-stannanes by Selenoxide Elimination

Vincent J. Jephcote and Eric J. Thomas *,†
The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, UK

The α-methyl-, α-phenyl- and α,α-dimethyl-allylstannanes **20–22** have been prepared by oxidative elimination of the corresponding primary selenides **17–19**, and were found to be stable with respect to 1,3-migration of the tributyltin moiety in non-polar solvents ($t \leqslant 100$ °C). Homoallylstannanes **32–34** were the major products obtained by oxidative elimination of the secondary selenides **29–31**, with mixtures of regioisomers being obtained from the other secondary selenides investigated.

Allylstannanes are useful in organic synthesis [1] as they undergo regio- and stereo-selective reactions with aldehydes under both Lewis acid and thermal conditions to give homoallylic alcohols,[2,3] and they react with alkyl and aryl halides *via* a free radical chain process to give alkenes.[4] Several procedures have been developed for the synthesis of allylstannanes, but for unsymmetric allylstannanes these either give the regioisomer **1** with the tin substituent at the less substituted end of the allyl fragment,[5] or they give mixtures of both the γ- and α-isomers **1** and **2**.[6]

Our interest in the chemistry of α-alkoxycrotylstannanes **3** (R = Me, R′ = OR″)[7] led us to investigate syntheses of other α-substituted allylstannanes. The α-ethoxyallylstannane **2** (R = OEt, R′ = Bu) has been prepared by treatment of (chloroethoxymethyl)tributylstannane with vinylmagnesium bromide, but was found to be unstable with respect to isomerization to vinyl ether **1** (R = OEt, R′ = Bu) on chromatography or when set aside at room temperature.[8] The α-methylallylstannane **2** (R = R′ = Me) was also found to be unstable with respect to isomerization to the crotylstannane **1** (R = R′ = Me).[9]



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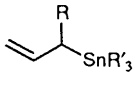

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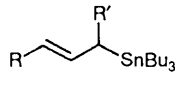

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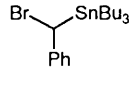

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Preliminary studies into the synthesis of the α-phenylcrotylstannane **3** (R = Me, R′ = Ph) by coupling propenylmagnesium bromide and the bromophenylmethylstannane **4** were not encouraging and so an alternative route to α-substituted allylstannanes was required. We now report a synthesis of α-substituted allylstannanes which is based on the effective synthesis of allylsilanes using selenoxide elimination.[10] Since our preliminary report,[11] an alternative regioselective synthesis of unsymmetric allystannanes has been described which is based upon aldol condensation and decarboxylative dehydration of trialkyltin substituted esters.[12]

Results and Discussion

To check the viability of the selenoxide approach to allylstannanes, 3-tributylstannylpropanol **5** was prepared from allyl alcohol and tributyltin hydride,[13] and converted into the 2-nitrophenyl selenide **6** using 2-nitrophenyl selenocyanate and tributylphosphine in tetrahydrofuran (THF).[14] Oxidative elimination was achieved using *m*-chloroperbenzoic acid and an excess of hydrogen peroxide in a water–dichloromethane two-phase system to provide propenyltributylstannane **7** (49% after chromatography).

5 X = OH
6 X = *o*-$NO_2C_6H_4Se$

7

The β-tributyltin esters **11–13** were prepared by addition of tributyltin lithium to the corresponding α,β-unsaturated esters **8–10**,[15] and were reduced using lithium aluminium hydride to give the primary alcohols **14–16**. Treatment of these with 2-nitrophenyl selenocyanate and tributylphosphine gave the corresponding selenides, which were oxidized using *m*-chloroperbenzoic acid, the excess of hydrogen peroxide not being required, to provide the α-substituted allylstannanes **20–22**. These were isolated in yields of 55–75% after flash chromatography on base washed silica.

8 R = Me, R′ = H
9 R = Ph, R′ = H
10 R = R′ = Me

11 R = Me, R′ = H
12 R = Ph, R′ = H
13 R = R′ = Me

20 R = Me, R′ = H
21 R = Ph, R′ = H
22 R = R′ = Me

14 R = Me, R′ = H, X = OH
15 R = Ph, R′ = H, X = OH
16 R = R′ = Me, X = OH
17 R = Me, R′ = H, X = SeAr
18 R = Ph, R′ = H, X = SeAr
19 R = R′ = Me, X = SeAr

Ar = *o*-$NO_2C_6H_4$–

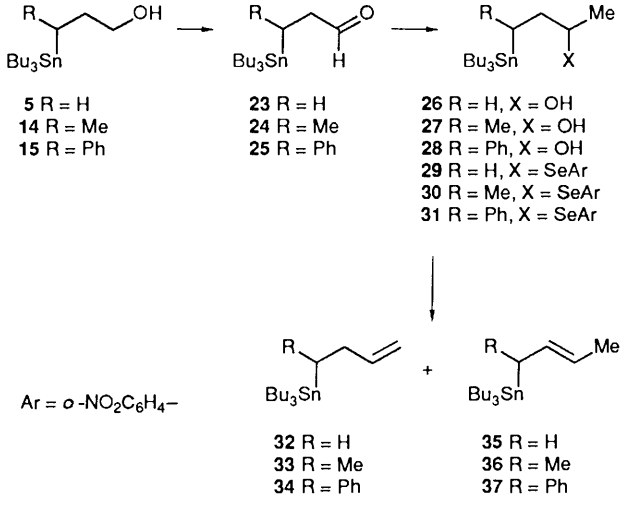
The α-substituted allylstannanes **20–22** were found to be reasonably stable with respect to 1,3-migration of the tributyltin substituent, at least in non-polar solvents over short periods of time. The α-methyl-and α,α-dimethyl-allylstannanes **20** and **22** were unaffected by heating in toluene under reflux for 21 h,

† *Present address:* The Department of Chemistry, The University of Manchester, Manchester M13 9PL UK.

although some decomposition was observed in xylene when heated under reflux. The α-phenylallylstannane **21** was less stable, *ca.* 25% decomposition and some isomerization taking place during heating in benzene under reflux for 22 h. However, much faster 1,3-isomerization of these stannanes was observed in methanol and in dichloromethane in the presence of a trace of BF_3·Et_2O. Isomerization was also observed on storing samples of the stannanes in solution, *e.g.* some 50% 1,3-isomerization was observed for stannane **20** on storing as a dilute solution in [$^2H_6$] benzene at room temperature for 14 d.

Next, the regioselectivity of oxidative elimination from a series of secondary trialkyltin substituted selenides was investigated to examine the suitability of this approach for the synthesis of α,γ-disubstituted allylstannanes.

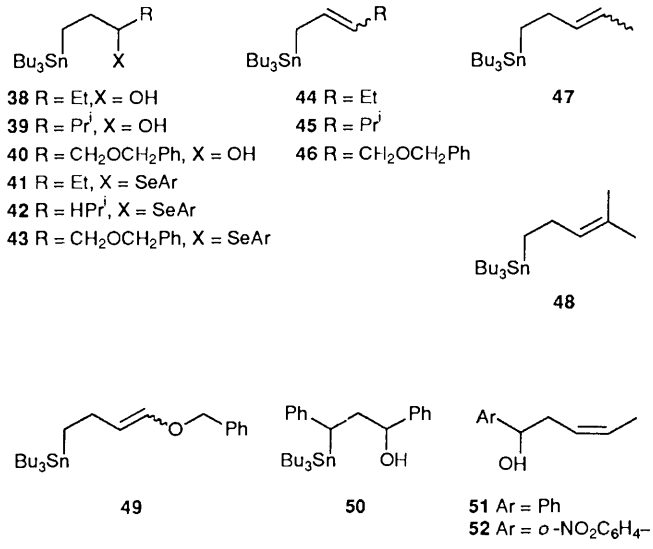
Oxidation of the 3-tributylstannyl alcohols **5**, **14** and **15**, using *N*-chlorosuccinimide gave the aldehydes **23**–**25**[16] which were treated with methyl magnesium iodide to give adducts **26**–**28**. In the cases of the α-methyl and α-phenyl stannanes **24** and **25**, the addition of the Grignard reagent gave mixtures of isomers, which were separated in the phenyl series. The Grignard products were then converted into the selenides **29**–**31** using 2-nitrophenyl selenocyanate and tributylphosphine, which were subjected to oxidative elimination under the standard conditions. The α-unsubstituted and α-phenyl stannyl selenides **29**



and **31** gave rise to the homoallyl stannanes **32** and **34** containing only traces of their allylic isomers **35** and **37**. The elimination from the α-methyl stannyl selenide was slightly less regioselective giving rise to a mixture of the homoallyl- and allylstannanes **33** and **36**, but again the homoallylic isomer **33** predominated, **33**–**36** (75:25).

3-(Tributylstannyl)propanal **23** was treated with ethylmagnesium bromide, isopropylmagnesium bromide and benzyloxymethyllithium to give rise to adducts **38**–**40** which were converted into the 2-nitrophenyl selenides **41**–**43** in the usual manner. Oxidative elimination from the pentan-3-yl selenide **41** was not regioselective and gave rise to a mixture of unsaturated stannanes presumably containing both the allyl-and homoallylstannanes **44** and **47** which could not be separated or properly characterized. Oxidative elimination from the 4-methylpentan-3-yl selenide **42** similarly gave rise to a mixture of products, but in this case the allylstannane **45** seemed to be the major component, ratio **45**–**48** *ca.* 60:40. The 1-benzyloxybutan-2-yl selenide **43** gave a mixture of the allyl-and homoallyl-stannanes **46** and **49** which were separated by flash chromatography to give the homoallylic stannane **49** (12%), as a 3:1 mixture of *E*- and *Z*-isomers, followed by the allylic stannane **46** (59%), also a mixture of *E*- and *Z*-isomers, ratio 85:15.

These results tend to suggest that the tributyltin substituent



has little effect on the regioselectivity of the selenoxide elimination, which tends to take place preferentially towards the carbon bearing the more acidic hydrogen. The 3-phenyl-3-tributylstannylpropanal was also treated with phenylmagnesium bromide to give the two diastereoisomers of 1,3-diphenyl-3-tributylstannylpropanol **50** which were separated by flash chromatography. However, conversion of these into the corresponding 2-nitrophenyl selenides using the usual procedure was complicated by the formation of side-products believed to be *cis*-and *trans*-1,2-diphenylcyclopropane and was not continued.

Finally the regioselectivity of reactions between the α-methyl allylstannane **20** and aldehydes was briefly examined. Unsymmetric allylstannanes have been found to give mixtures of products with alkyl halides under free radical conditions,[17] but there is one reference to a regioselective reaction of stannane **20** with benzaldehyde under Lewis Acid catalysed conditions.[18] It was found that heating mixtures of the α-methylallylstannane **20** and either benzaldehyde or *p*-nitrobenzaldehyde, gave reasonable yields of the *Z*-1-arylpent-3-enols **51** and **52**. The *Z* stereochemistry of these products was established by their 3-H–4-H coupling constants (*ca.* 11 Hz) and by NOE studies including the observation of enhancements of the peak due to 1-H (2–3%) on irradiation of the terminal methyl group. However under Lewis acid (BF_3·Et_2O) catalysed conditions, mixtures of products were obtained in our hands using stannane **20** and benzaldehyde and it would appear that 1,3-isomerization of the stannane had competed with the reaction with the aldehyde in this case.[18]

Experimental

IR spectra were measured on Perkin-Elmer 257 and 681 spectrophotometers as liquid films unless otherwise stated. NMR spectra were recorded on a Bruker WH 300 spectrometer using [^{2}H]chloroform as solvent and all *J* values are in Hz. Mass spectra were measured on a VG Micromass 16F spectometer using either electron impact (EI) or chemical ionization (CI) modes. Characteristic isotope clusters were observed for organotin and selenium compounds with those corresponding to ^{120}Sn and ^{80}Se being quoted. M.p.s were determined on a Buchi 510 apparatus.

Short column and flash chromatography were carried out on Merck Kieselgel 60H and silica gel 60, respectively. Base washed silica was prepared by washing flash silica with saturated aqueous $KHCO_3$ and then with distilled water until neutral, followed by drying at 170 °C for several days.

All solvents were dried and distilled before use. Ether refers to diethyl ether, and light petroleum to the fraction boiling between 40 and 60 °C. Lithium diisopropylamide (LDA) was prepared from equimolar amounts of butyllithium in hexane and anhydrous diisopropylamine in THF under an atmosphere of nitrogen at 0 °C. Tributyltin hydride was prepared according to a literature procedure,[19] and was converted into tributyltin lithium using an equimolar amount of LDA in THF–hexane under an atmosphere of nitrogen at 0 °C. 3-Tributylstannylpropanal **23**; ν_{max}/cm^{-1} 1722; δ_H 2.65 [2 H, m, C(2)-H_2] and 9.75 (1 H, narrow t, CHO); *m/z* (EI) 291 ($M^+ - 57$); was prepared following the literature procedure from 3-tributylstannylpropanol using *N*-chlorosuccinimide–triethylamine.[16]

Preparation of 3-Tributylstannyl Esters.—The unsaturated ester (*ca.* 10 mmol) was added to a solution of tributyltin lithium (10 mmol) in THF–hexane at −78 °C under an atmosphere of nitrogen, followed by saturated aqueous ammonium chloride (20 ml). The reaction mixture was warmed to room temperature and partitioned between water (30 ml) and ether (30 ml). The organic phase was dried ($MgSO_4$), and concentrated under reduced pressure. The residue was flash chromatographed using ether–light petroleum as eluent to give the product.

Methyl 3-tributylstannylbutanoate **11** (30%), a pale yellow oil (Found: $M^+ - C_4H_9$ 335.1033. $C_{13}H_{27}O_2{}^{120}Sn$ requires M, 335.1033); ν_{max}/cm^{-1} 1735, 1198, 1178, 1070 and 1002; δ_H 0.75–0.95 (15 H, m), 1.21 (3 H, d, *J* 8, CH*Me*), 1.25–1.7 (13 H, complex m), 2.47 (1 H, dd, *J* 8 and 14, 2-H), 2.53 (1 H, dd, *J* 6 and 14, 2-H) and 3.60 (3 H, s, OMe); *m/z* (EI) 335 ($M^+ - 57$, 100%).

Methyl 3-phenyl-3-tributylstannylpropanoate **12** (58%), a pale yellow oil (Found: $M^+ - C_4H_9$ 397.1190. $C_{18}H_{29}O_2{}^{120}Sn$ requires M, 397.1189); ν_{max}/cm^{-1} 3025, 1737, 1600, 1492, 1198 and 1168; δ_H 0.7–0.95 (15 H, m), 1.15–1.5 (12 H, m), 2.8–3.2 (3 H, m, $CHCH_2$), 3.62 (3 H, s, OMe) and 6.95–7.3 (5 H, m, aromatic H).

Methyl 3-methyl-3-tributylstannylbutanoate **13** (25%), a pale yellow oil (Found: $M^+ - C_4H_9$349.1190. $C_{14}H_{20}O^{120}Sn$ requires M. 349.1189); ν_{max}/cm^{-1} 1735, 1200, 1179, 1130 and 1018; δ_H 0.75–0.95 (15 H, m), 1.17 (6 H, s, 2 × Me), 1.2–1.55 (12 H, m), 2.35 (2 H, s, C(2)-H_2) and 3.65 (3 H, s, OMe); *m/z* (EI) 349 ($M^+ - 57$, 100%).

Reduction of 3-Tributylstannyl Esters.—A solution of the 3-tributylstannyl ester **11**–**13** in ether was added dropwise to a suspension of lithium aluminium hydride (*ca.* 1 mol equiv.) in ether at 0 °C under an atmosphere of nitrogen and the mixture heated under reflux for 4 h. After the mixture had cooled saturated aqueous NH_4Cl was added, the mixture filtered and the organic phase washed with water and dried ($MgSO_4$). Concentration under reduced pressure left an oil which was distilled to give the product (bath temperatures given).

3-Tributylstannylbutan-1-ol **14** (75%) had b.p. 200 °C at 1 mmHg (lit.,[20] b.p. 131 °C at 0.5 mmHg); ν_{max}/cm^{-1} 3320 and 1045; δ_H 3.68 (2 H, q, *J* 7, CH_2OH); *m/z* (EI) 307 ($M^+ - 57$, 100%).

3-*Phenyl*-3-*tributylstannylpropan*-1-*ol* **15** (71%), b.p. 250 °C at 2 mmHg, was a colourless oil (Found: $M^+ - C_4H_9$, 369.1239. $C_{17}H_{29}O^{120}Sn$ requires M, 369.1240); ν_{max}/cm^{-1} 3320, 3075, 3055, 3020, 1600, 1490, 1072 and 1030; δ_H 0.65–1.0 (15 H, m), 1.15–1.5 (13 H, m), 2.12 and 2.33 (each 1 H, m, 2-H), 2.68 (1 H, dd, *J* 6, 11, 3-H), 3.6 (2 H, m, CH_2OH) and 6.95–7.4 (5 H, m, aromatic H).

3-*Methyl*-3-*tributylstannylbutan*-1-*ol* **16** (73%), b.p. 230 °C at 1 mmHg, was a colourless oil (Found: $M^+ - C_4H_9$, 321.1242. $C_{13}H_{29}O^{120}Sn$ requires M, 321.1240); ν_{max}/cm^{-1} 3310, 1060 and 1018; δ_H 0.75–0.95 (15 H, m), 1.15 (6 H, s, 2 × Me), 1.2–1.35 (13 H, m) and 1.71 and 3.68 (each 2 H, m); *m/z* (EI) 321 ($M^+ - 57$, 100%).

3-*Tributylstannylbutanal* **24**.—3-Tributylstannylbutan-1-ol **14** (4.22 g, 11.6 mmol) was added dropwise to a mixture of *N*-chlorosuccinimide (3.1 g, 23.2 mmol) and dimethyl sulphide (1.71 ml, 23.2 mmol) in toluene (75 ml) at −23 °C.[16] The mixture was stirred for 3 h, triethylamine (23.2 mmol) was added dropwise, and, after 20 min, the mixture was warmed to 0 °C and quenched by the addition of aqueous NH_4Cl. The mixture was diluted with ether (100 ml), washed successively with brine and water, dried (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica eluting with ether–light petroleum (1:40) gave the *title compound* **24** (2.39 g, 57%), as a pale yellow oil; ν_{max}/cm^{-1} 1722, 1455, 1377 and 1070; δ_H 0.75–0.95 (15 H, m), 1.15–1.66 (13 H, m), 1.2 (3 H, d, *J* 8, CH*Me*), 2.53 (1 H, ddd, *J* 17, 8 and 2, 2-H), 2.6 (1 H, ddd, *J* 17, 7 and 1, 2-H) and 9.73 (1 H, narrow m, 1-H); *m/z* (EI) 305 ($M^+ - 57$, 80%).

3-*Phenyl*-3-*tributylstannylpropanal* **25**.—3-Phenyl-3-tributylstannylpropan-1-ol **15** (4.07 g, 9.6 mmol) was treated with *N*-chlorosuccinimide (2.56 g, 19.2 mmol), dimethyl sulphide (1.40 ml, 19.2 mmol) and triethylamine (2.67 ml, 19.2 mmol) in toluene as described above, to give the *title compound* **25** (2.48 g, 61%) as a pale yellow oil; ν_{max}/cm^{-1} 3080, 3060, 3025, 2715, 1720, 1600, 1491, 1070, 760 and 699; δ_H 0.65–0.95 (15 H, m), 1.15–1.5 (12 H, m), 2.85–3.22 [3 H, overlapping m, C(2)-H_2 and 3-H], 7.0 (3 H, m, aromatic H), 7.2 (2 H, m, aromatic H) and 9.7 (1 H, narrow m, 1-H); *m/z* (EI) 367 ($M^+ - 57$, 7%).

4-*Tributylstannylbutan*-2-*ol* **26**.—A solution of 3-tributylstannylpropanal **23** (1.98 g, 5.7 mmol) in ether (2 ml) was added to a solution of freshly prepared methylmagnesium iodide (6.3 mmol) in ether (8 ml) at 0 °C under an atmosphere of nitrogen. The mixture was heated under reflux for 30 min, cooled to 0 °C and quenched by the addition of aqueous NH_4Cl (10 ml). The organic layer was diluted using ether, separated, washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ether–light petroleum (1:5) as eluent gave the *title compound* **26** (580 mg, 28%) as a colourless oil; ν_{max}/cm^{-1} 3325, 1110, 1068 and 1018; δ_H 0.65–1.0 (15 H, m), 1.2 (3 H, d, *J* 7 Hz, CH*Me*), 1.18–1.6 (17 H, m) and 3.66 (1 H, m, 2-H); *m/z* (EI) 307 ($M^+ - 57$, 100%).

4-*Tributylstannylpentan*-2-*ol* **27**.—3-Tributylstannylbutanal **24** (1.2 g, 3.3 mmol) was treated with methylmagnesium iodide (3.6 mmol) as described above to give the *title compound* **27** (920 mg, 73%), as a mixture of diastereoisomers (Found: $M^+ - C_4H_9$ 321.1242. $C_{13}H_{29}O^{120}Sn$ requires M, 321.1240); ν_{max}/cm^{-1} 3340 and 1068; δ_H 0.71–1.0 (15 H, m), 1.1–1.8 (22 H, m) and 3.88 (1 H, m, 2-H); *m/z* (EI) 321 ($M^+ - 57$, 100%).

4-*Phenyl*-4-*tributylstannylbutan*-2-*ol* **28**.—3-Phenyl-3-tributylstannylpropanal **25** (1.183 g, 2.8 mmol) was treated with methylmagnesium iodide (3.1 mmol) as described above to give the *title compound* **28** (840 mg, 68%) as a mixture of diastereoisomers which were separated by flash chromatography using ether–light petroleum as eluent. The *less polar diastereoisomer* **28a** was an oil (Found: $M^+ - C_4H_9$, 383.1397. $C_{18}H_{31}O^{120}Sn$ requires M, 383.1397); ν_{max}/cm^{-1} 3350, 1600, 1490, 1125, 1072, 763 and 700; δ_H 0.65–1.0 (15 H, m), 1.16 [3 H, d, *J* 6 C(1)-H_3], 1.15–1.55 (13 H, m), 1.85 (1 H, ddd, *J* 15, 10 and 5, 3-H), 2.24 (1 H, ddd, *J* 15, 12 and 2, 3-H), 2.83 (1 H, dd, *J* 12 and 5, 4-H), 3.72 (1 H, m, 2-H), 7.01 (3 H, m, aromatic H) and 7.27 (2 H, m, aromatic H); *m/z* (EI) 383 ($M^+ - 57$, 65%). The *more polar diastereoisomer* **28b** was also an oil (Found: $M^+ - C_4H_9$, 383.1397. $C_{18}H_{31}O^{120}Sn$ requires M, 383.1397); ν_{max}/cm^{-1} 3360, 3100, 3080, 3040, 1620, 1502, 1080, 947, 773 and 710; δ_H 0.65–0.95 (15 H, m), 1.1–1.55 (16 H, m), 1.87 and 2.38 (each 1 H, m, 3-H), 2.64 (1 H, dd, *J* 13 and 6, 4-H), 3.76 (1 H, m, 2-H) and 6.95–7.27 (5 H, m, aromatic H); *m/z* 383 ($M^+ - 57$, 35%).

1-*Tributylstannylpentan*-3-*ol* **38**.—3-Tributylstannylpropanal **23** (2g, 5.7 mmol) was treated with ethylmagnesium bromide (6.3 mmol) as described above to give the *title compound* **38** (1.58 g, 73%) as a colourless oil (Found: $M^+ - C_4H_9$, 321.1239. $C_{13}H_{29}O^{120}Sn$ requires M, 321.1240); ν_{max}/cm^{-1} 3325, 1067 and 958 δ_H 0.6–1.0 (20 H, m), 1.2–1.75 (17 H, m) and 3.4 (1 H, m, 3-H); *m/z* (EI) 321 ($M^+ - 57$, 100%).

4-*Methyl*-1-*tributylstannylpentan*-3-*ol* **39**.—3-Tributylstannylpropanal **23** (2g, 5.7 mmol) was treated with propan-2-ylmagnesium chloride (6.3 mmol) as described above to give the *title compound* **39** (1.6 g, 72%) as a colourless oil (Found: $M^+ - C_4H_9$, 335.1398. $C_{14}H_{31}O^{120}Sn$ requires *M*, 335.1397); ν_{max}/cm^{-1} 3350, 1068, 998 and 980; δ_H 0.6–1.8 (39 H, m) and 3.24 (1 H, m, 3-H); *m/z* (EI) 335 ($M^+ - 57$, 100%).

1-*Phenylmethoxy*-4-*tributylstannylbutan*-2-*ol* **40**.—Butyllithium (2.82 ml of a 1.63 mol dm^{-3} solution in hexane, 4.6 mmol) was added to a solution of (phenylmethoxymethyl)tributylstannane[21] (1.97 g, 4.6 mmol) in THF (20 ml) at −78 °C under an atmosphere of nitrogen, followed by 3-tributylstannylpropanal (1.51 g, 4.4 mmol). After 5 min, the mixture was allowed to warm to 0 °C and was quenched by the addition of saturated, aqueous NH_4Cl (20 ml). The mixture was diluted with ether (50 ml), separated and the organic layer washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography of the residue on silica using ethyl acetate–light petroleum (1:15) as eluent gave the *title compound* **40** (1.41 g, 69%) as a pale yellow oil (Found: $M^+ - C_4H_9$, 413.1503. $C_{19}H_{33}O_2{}^{120}Sn$ requires M, 413.1502); ν_{max}/cm^{-1} 3430, 3060, 3025, 1097, 733 and 696; δ_H 0.65–0.97 (15 H, m), 1.2–1.7 (16 H, m), 2.33 (1 H, d, *J* 4, OH), 3.37 (1 H, dd, *J* 10 and 8, 1-H), 3.57 (1 H, dd, *J* 10 and 2, 1-H), 3.71 (1 H, m, 2-H), 4.57 (2 H, s, OCH_2Ph) and 7.35 (5 H, m, aromatic H); *m/z* (EI) 413 ($M^+ - 57$, 70%).

1,3-*Diphenyl*-3-*tributylstannylpropanol* **50**.—3-Phenyl-3-tributylstannylpropanal **25** (1.15 g, 2.7 mmol) was treated with phenylmagnesium bromide as described above to give the *title compound* **50** (1.2 g, 88%) as a mixture of diastereoisomers which were separated by flash chromatography. The *less polar diastereoisomer* **50a** was isolated as an oil (Found: $M^+ - C_4H_9$, 445.1555. $C_{23}H_{33}O^{120}Sn$ requires M, 445.1552); ν_{max}/cm^{-1} 3420, 3060, 3025, 1597, 1492, 1067, 1024, 760 and 700; δ_H 0.65–1.0 (15 H, m), 1.11–1.15 (12 H, m), 1.79 (1 H, d, *J* 5, OH), 2.14 (1 H, ddd, *J*, 5, 10 and 15 Hz, 2-H), 2.44 (1 H, m, 2-H), 3.01 (1 H, dd, *J* 5 and 13, 3-H), 4.62 (1 H, m, 1-H) and 7.0–7.45 (10 H, m, aromatic H); *m/z* (EI) 443 ($M^+ - 59$, 40%). The *more polar diastereoisomer* **50b** was also an oil (Found: $M^+ - C_4H_9$ 445.1555. $C_{23}H_{33}O^{120}Sn$ requires *M*, 445.1552); ν_{max}/cm^{-1} 3360, 3062, 3024, 1597, 1492, 1007, 761 and 700; δ_H 0.63–0.95 (15 H, m), 1.12–1.54 (12 H, m), 1.82 (1 H, d, *J* 3, OH), 2.19 (1 H, ddd, *J* 12, 8 and 4, 2-H), 2.33 (1 H, dd, *J* 12 and 4, 3-H), 2.71 (1 H, m, 2-H), 4.6 (1 H, m, 1-H) and 7.0–7.45 (10 H, m, aromatic H); *m/z* (EI) 443 ($M^+ - 59$, 60%).

Preparation of 2-*Nitrophenyl Selenides*.—Tributylphosphine (1.1 mol equiv.) was added to a solution of the alcohol and 2-nitrophenyl selenocyanante (1.1 mol equiv.) in THF and the mixture was stirred at room temperature for 2–4 h. After concentration under reduced pressure, flash chromatography of the residue using ether–light petroleum as eluent gave the following selenides:

2-*Nitrophenyl* 3-*tributylstannylpropyl selenide* **6** (60%), a yellow oil; ν_{max}/cm^{-1} 1588, 1562, 1509, 1330, 1300, 908 and 730; δ_H 0.75–1.9 (17 H, m), 1.2–1.6 (12 H, m), 1.95 and 2.94 (each 2 H, m), 7.3 (1 H, m, aromatic H), 7.5 (2 H, m, aromatic H) and 8.28 (1 H, d, *J* 7, aromatic H); *m/z* (CI) 553 ($M^+ + 18$, 50%), 478 ($M^+ - 57$, 80%), 448 ($M^+ - 87$, 80%).

2-*Nitrophenyl* 3-*tributylstannylbutyl selenide* **17**. (66%), a yellow oil; ν_{max}/cm^{-1} 1590, 1565, 1511, 1332, 1303, 1250, 1038 and 730; δ_H 0.75–1.0 (15 H, m), 1.2–1.55 (16 H, m), 1.85–2.16 [2 H, m, C(2)-H_2], 2.92 and 3.04 (each 1 H, m, 1-H), 7.32 (1 H, m, aromatic H), 7.52 (2 H, m, aromatic H) and 8.3 (1 H, d, *J* 8, aromatic H); *m/z* (CI) 567 ($M^+ + 18$, 25%), 462 ($M^+ - 87$, 100%).

2-*Nitrophenyl* 3-*phenyl*-3-*tributylstannylpropyl selenide* **18** (63%), a yellow oil; ν_{max}/cm^{-1} 3078, 3057, 3020, 1590, 1565, 1511, 1490, 1330, 1302, 1039, 730 and 700; δ_H 0.7–0.95 (15 H, m), 1.17–1.5 (12 H, m), 2.25 and 2.52 (each 1 H, m, 2-H), 2.74 (2 H, m, 1-H and 3-H), 3.98 (1 H, m, 1-H), 7.0–7.48 (8 H, m, aromatic H) and 8.26 (1 H, d, *J* 7, aromatic H); *m/z* (CI) 630 ($M^+ + 18$, 35%).

3-*Methyl*-3-*tributylstannylbutyl* 2-*nitrophenyl selenide* **19** (57%), a yellow oil; ν_{max}/cm^{-1} 1590, 1564, 1511, 1331, 1304 and 730; δ_H 0.75–1.0 (15 H, m), 1.22 (6 H, s, 2 × Me), 1.2–1.6 (12 H, m), 1.87 and 2.89 [each 2 H, m, 2- and C(1)-H_2], 7.3 (1 H, m, aromatic H), 7.5 (2 H, m, aromatic H) and 8.3 (1 H, d, *J* 7, aromatic H); *m/z* (CI) 581 ($M^+ + 18$, 3%), 506 ($M^+ - 57$, 30%) and 476 ($M^+ - 87$, 100%).

2-*Nitrophenyl* 4-*tributylstannylbutan*-2-*yl selenide* **29** (43%); ν_{max}/cm^{-1} 1589, 1562, 1510, 1330, 1303 and 730; δ_H 0.7–2.05 (34 H, m), 3.4 (1 H, m, 2-H) and 7.31, 7.5, 7.57 and 8.3 (each 1 H, m, aromatic H); *m/z* (CI) 567 ($M^+ + 18$, 10%).

2-*Nitrophenyl* 4-*tributylstannylpentan*-2-*yl selenide* **30** (75%), a yellow oil; ν_{max}/cm^{-1} 1590, 1566, 1512, 1333, 1304 and 730; δ_H 0.72–1.05 (15 H, m), 1.22–1.63 (19 H, m), 1.85 and 2.00 (each 1 H, m, 3-H), 3.6 (1 H, m, 2-H) and 7.31, 7.49, 7.58 and 8.25 (each 1 H, m, aromatic H); *m/z* (CI) 580 ($M^+ + 18$, 50%) and 505 ($M^+ - 58$, 100%).

2-*Nitrophenyl* 4-*phenyl*-4-*tributylstannylbutan*-2-*yl selenide* **31** (60%), a mixture of diastereoisomers (Found: $M^+ - C_4H_9$, 568.0776. $C_{24}H_{34}NO_2{}^{80}Se^{120}Sn$ requires *M*, 568.0777); ν_{max}/cm^{-1} 3042, 1602, 1578, 1528, 1503, 742 and 711; δ_H 0.65–0.98 (15 H, m), 1.13–1.55 (15 H, m), 1.85–3.0 (3 H, overlapping m, 3-H and 4-H of both diastereoisomers), 3.4 (1 H, m, 2-H), 6.95–7.45 (8 H, m, aromatic H) and 8.2 (1 H, m, aromatic H); *m/z* (EI) 568 ($M^+ - 57$, 60%).

2-*Nitrophenyl* 1-*tributylstannylpentan*-3-*yl selenide* **41** (60%), a yellow oil; ν_{max}/cm^{-1} 1587, 1561, 1510, 1330, 1300 and 729; δ_H 0.7–2.0 (36 H, m), 3.31 (1 H, q, *J* 6, 3-H), 7.3 (1 H, m, aromatic H), 7.42–7.6 (2 H, m, aromatic H) and 8.29 (1 H, m, aromatic H); *m/z* (CI) 581 ($M^+ + 18$, 10%) and 506 ($M^+ - 57$, 100%).

4-*Methyl*-1-*tributylstannylpentan*-3-*yl* 2-*nitrophenyl selenide* **42** (63%), a yellow oil; ν_{max}/cm^{-1} 1587, 1562, 1510, 1330, 1300 and 730; δ_H 0.7–1.0 (17 H, complex m), 1.06 (6 H, d, *J* 7, $CHMe_2$), 1.2–1.6 (12 H, m), 1.85–2.05 (2 H, m), 2.19 (1 H, m), 3.25 (1 H, m, 3-H) and 7.3, 7.48, 7.6 and 8.29 (each 1 H, m, aromatic H); *m/z* (CI) 595 ($M^+ + 18$, 20%) and 520 ($M^+ - 57$, 100%).

1-*Benzyloxy*-4-*tributylstannylbutan*-2-*yl* 2-*nitrophenyl selenide* **43** (85%), a yellow oil; ν_{max}/cm^{-1} 3080, 3060, 3025, 1588, 1562, 1510, 1330, 1301, 1250, 1092 and 729; δ_H 0.7–1.05 (17 H, complex m), 1.2–1.6 (12 H, m), 1.9 and 2.15 (each 1 H, m), 3.5 (1 H, m, 2-H), 3.75 (2 H, d, *J* 7, C(1)-H_2), 4.56 and 4.58 (each 1 H, d, *J* 12, *H*CHPh), 7.3 (6 H, m, aromatic H) and 7.42, 7.57 and 8.22 (each 1 H, m, aromatic H); *m/z* (CI) 673 ($M^+ + 18$, 80%).

Prop-2-*enyl*(*tributyl*)*stannane* **7**.—Aqueous hydrogen peroxide (100 vol.; 0.5 ml) and *m*-chloroperbenzoic acid (105 mg, 0.6 mmol) in dichloromethane (2 ml) were added to a stirred solution of the 2-nitrophenyl 3-tributylstannylpropyl selenide **6** (270 mg, 0.51 mmol) in dichloromethane (10 ml) at −60 °C. After 75 m, the reaction mixture was allowed to warm to room temperature and was poured into aqueous $NaHCO_3$ (10 ml). The layers were separated and the organic layer washed with water, dried ($NaSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue on base washed silica, using light petroleum as eluent, gave the *title compound* **7**[22] (82

mg, 49%), as a pale, yellow oil; ν_{max}/cm^{-1} 3075, 1620 and 880; δ_H 0.75–1.0 (1.5 H, m), 1.2–1.6 (12 H, m), 1.78 [2 H, d, *J* 8, C(1)-H_2], 4.59–4.9 [2 H, m, C(3)H_2] and 5.95 (1 H, m, 2-H); *m/z* (EI) 291 ($M^+ - 41$, 22%).

General Procedure for Preparation of Allylstannanes.—*m*-Chloroperbenzoic acid (1 mol equiv.) was added to a rapidly stirred mixture of a solution of the selenide in dichloromethane and aqueous $NaHCO_3$ (5 mol equiv.). After stirring the mixture for *ca.* 6 h, the organic phase was separated, washed with water, dried quickly (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography of the residue on base washed silica, using light petroleum as eluent, gave the following allylstannanes.

But-3-en-2-yl(tributyl)stannane **20** (74%), a colourless oil (Found: $M^+ - C_4H_9$, 291.1132. $C_{12}H_{27}{}^{120}Sn$ requires *M*, 291.1135); ν_{max}/cm^{-1} 3079, 1616 and 877; δ_H 0.75–1.0 (15 H, m), 1.18–1.6 (15 H, m), 2.18 (1 H, m, 2-H), 4.62–4.78 [2 H, m, C(4)-H_2] and 6.11 (1 H, m, 3-H); *m/z* (EI) 288 ($M^+ - 58$, 45%) and 177 ($M^+ - 169$, 100%).

1-Phenylprop-2-enyl(tributyl)stannane **21** (56%), a colourless oil (Found: $M^+ - C_4H_9$, 351.1134. $C_{17}H_{27}{}^{120}Sn$ requires *M*, 351.1135); ν_{max}/cm^{-1} 3075, 3058, 3020, 1619, 1597, 1489, 1376, 1193, 1070, 882, 759 and 698; δ_H 0.7–1.0 (15 H, m), 1.17–1.6 (12 H, m), 3.55 (1 H, d, *J* 10, 1-H), 4.72–5.0 [2 H, m, C(3)H_2], 6.32 (1 H, dt, *J* 15 and 10, 2-H), 7.05 (3 H, m, aromatic H) and 7.22 (2 H, m, aromatic H).

1-Methylbut-3-en-2-yl(tributyl)stannane **22** (58%), a colourless oil (Found: $M^+ - C_4H_9$, 303.1136. $C_{13}H_{27}{}^{120}Sn$ requires *M*, 303.1135); ν_{max}/cm^{-1} 3080, 1611 and 870; δ_H 0.72–1.0 (15 H, m), 1.25 (6 H, s, 2 × Me), 1.22–1.6 (12 H, m), 4.5–4.75 [2 H, m, C(4)-H_2] and 6.05 (1 H, dd, *J* 10 and 15, 3-H).

But-3-enyl(tributyl)stannane **32**.—Oxidation of 2-nitrophenyl 4-tributylstannylbutan-2-yl selenide **29** (145 mg, 0.26 mmol) using aqueous hydrogen peroxide and *m*-chloroperbenzoic acid (55 mg, 0.32 mmol) was carried as described above to give the *title compound*[23] **32** (57 mg, 63%), a colourless oil; ν_{max}/cm^{-1} 3075, 1636, 1374, 1069, 990 and 909; δ_H 0.7–1.0 (17 H, m), 1.23–1.6 (12 H, m), 2.25 [2 H, m, C(2)-H_2], 4.95 [2 H, m, C(4)-H_2] and 5.89 (1 H, m, 3-H); *m/z* (EI) 289 ($M^+ - 57$, 55%).

1-Phenylbut-3-enyl(tributyl)stannane **34**.—2-Nitrophenyl 4-phenyl-4-tributylstannylbutan-2-yl selenide **31** (190 mg, 0.3 mmol) was oxidized using *m*-chloroperbenzoic acid (58 mg, 0.33 ml) as described above to give the *title compound* **34** (42 mg, 33%) as a colourless oil (Found: $M^+ - C_4H_9$ 365.1291. $C_{18}H_{29}{}^{120}Sn$ requires M, 365.1291); ν_{max}/cm^{-1} 3101, 3080, 3041, 1650, 1611, 1503, 770 and 710; δ_H 0.75–1.0 (15 H, m), 1.15–1.53 (12 H, m), 2.55–2.9 [3 H, overlapping m, C(2)-H_2 and 1-H], 4.9–5.1 [2 H, m, C(4)-H_2], 5.78 (1 H, m, 3-H), 7.01 (3 H, m, aromatic H) and 7.19 (2 H, m, aromatic H); *m/z* (EI) 365 ($M^+ - 57$, 20%).

Oxidation of 1-Benzyloxy-4-tributylstannylbutan-2-yl 2-Nitrophenyl Selenide **43**.—The selenide **43** (275 mg, 0.42 mmol) was oxidized as described above using *m*-chloroperbenzoic acid (80 mg, 0.46 mmol) and $NaHCO_3$ (177 mg, 3 mmol) in dichloromethane–water. Flash chromatography of the crude product using ether–light petroleum as eluent gave two fractions. The less polar fraction was identified as *4-benzyloxybut-3-enyl(tributyl)stannane* **49** (24 mg, 12%), a colourless oil, a 3:1 mixture of geometrical isomers; ν_{max}/cm^{-1} 3020, 1645, 1212, 1180, 758 and 696; δ_H 0.7–1.05 (17 H, m), 1.22–1.64 (12 H, m), 2.17 [1.5 H, m, C(2)-H_2 of the major isomer], 2.35 [0.5 H, m, C(2)-H_2 of the minor isomer], 4.42 (0.25 H, m, 3-H of the minor isomer), 4.71 (1.5 H, s, OCH_2 of the major isomer), 4.8 (0.5 H, s, OCH_2 of the minor isomer), 4.93 (0.75 H, m, 3-H of the major isomer), 5.97 (0.25 H, d, *J* 6, 4-H of the minor isomer), 6.35 (0.75 H, d, *J* 12, 4-H of the major isomer) and 7.35 (5 H, m, aromatic H). The more polar fraction was identified as *4-benzyloxybut-2-enyl(tributyl)stannane* **46** (113 mg, 59%), an oil, the *E* isomer containing *ca.* 15% of its *Z*-diastereoisomer; ν_{max}/cm^{-1} 3080, 3060, 3020, 1646, 1068, 961, 732 and 698; δ_H 0.75–1.05 (15 H, m), 1.23–1.64 (12 H, m), 1.75–1.84 [2 H two overlapping d, *J* 8, C(1)-H_2 of both isomers], 3.99 [1.7 H, d, *J* 8, C(4)-H_2 of major isomer], 4.09 [0.3 H, d, *J* 6, C(4)-H_2 of minor isomer], 4.5 (1.7 H, s, OCH_2Ph of major isomer), 4.55 (0.3 H, s, OCH_2Ph of minor isomer), 5.44 and 5.89 (both 1 H dt, *J* 15 and 7 Hz, vinylic H) and 7.25–7.45 (5 H, m, aromatic H).

Reactions of But-3-en-2-yl(tributyl)stannane **20** *with Aldehydes.*—Stannane **20** (160 mg, 0.46 mmol) and freshly recrystallized 4-nitrobenzaldehyde (70 mg, 0.46 mmol) were mixed and heated together under an atmosphere of argon at 70 °C for 15 h. The mixture was cooled and upon flash chromatography using ether acetate–light petroleum (1:10) as eluent gave (*Z*)-*1-(4-nitrophenyl)pent-3-en-1-ol* **52** (67 mg, 69%) as a pale yellow oil; ν_{max}/cm^{-1} 3420, 3120, 3085, 3028, 1662, 1610, 1520, 1350, 1112, 1060, 1018, 860, 782, 760 and 706; δ_H 1.58 (3 H, d, *J* 6, CH_3), 2.39 (1 H, d, *J* 3, OH), 2.53 [2 H, m, C(2)-H_2] 4.84 (1 H, m, 1-H), 5.4 and 5.69 (each 1 H, m, vinylic H) and 7.53 and 8.17 (each 2 H, m, aromatic H); *m/z* (EI) 207 (M^+, 3%) and 152 ($M^+ - 55$, 100%).

Similarly benzaldehyde gave (*Z*)-1-phenylpent-3-en-1-ol **51** (40%); δ_H 1.62 (3 H, d, *J* 7, CH_3), 2.0 (1 H, d, *J* 3, OH), 2.42–2.65 [2 H, m, C(2)-H_2], 4.74 (1 H, m, 1-H), 5.43 and 5.64 (each 1 H, m, vinylic H) and 7.25–7.45 (5 H, m, aromatic H); *m/z* (EI) 162 (M^+, 15%) and 107 ($M^+ - 55$, 100%).

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