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# STEREOSPECIFIC CYCLOPROPANE SYNTHESIS FROM γ-STANNYL ALCOHOLS

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## Summary

γ-Stannyl tertiary alcohols and γ-stannyl benzyl alcohols form cyclopropanes stereospecifically on treatment with acid, with inversion of configuration at both carbon atoms.

## Introduction

In a preliminary communication [1] we reported that γ-stannyl tertiary and benzylic alcohols form cyclopropanes when treated with acid, reacting with inversion at both carbon atoms (via a "W" conformation). This is in contrast to γ-silyl tertiary alcohols which undergo a silicon-controlled carbonium ion rearrangement [2]. There was, however, ample precedent to indicate that the corresponding tin compounds would give cyclopropanes [3–5]. This work, including experimental details, is described in full in this paper.

## Results and discussion

The simplest pair of tertiary alcohols (**1**) and (**3**) illustrate the striking difference between silicon and tin. The γ-silyl alcohol **1** was known [2] to give the alkene **2** on treatment with acid. In contrast, the corresponding tin alcohol **3**, which we synthesized by the conjugate addition (**5** → **6**) of trimethyltin-lithium [6,7], gave the cyclopropane **4** exclusively.

Following the success of this reaction, we prepared the alcohols shown in Scheme 2, introducing the tin by hydrostannation [8]. Together, conjugate addition of trialkyltin-lithium and hydrostannation allowed us to synthesise a wide range of γ-stannyl alcohols. The reaction of each of the alcohols **8**, **10**, **12** and **13** with acid gave the corresponding cyclopropanes **14**, **15**, **16** and **17**, as shown in Scheme 3. These reactions demonstrate two important features of the cyclopropane-forming reaction. First, even if there is a good migrator in the β-position (a phenyl group in

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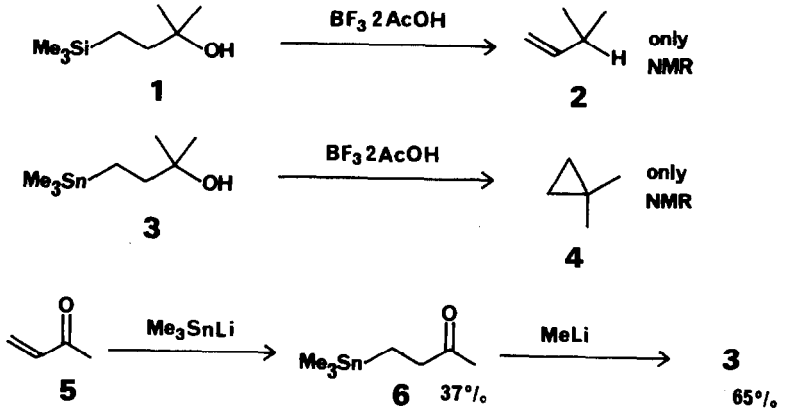
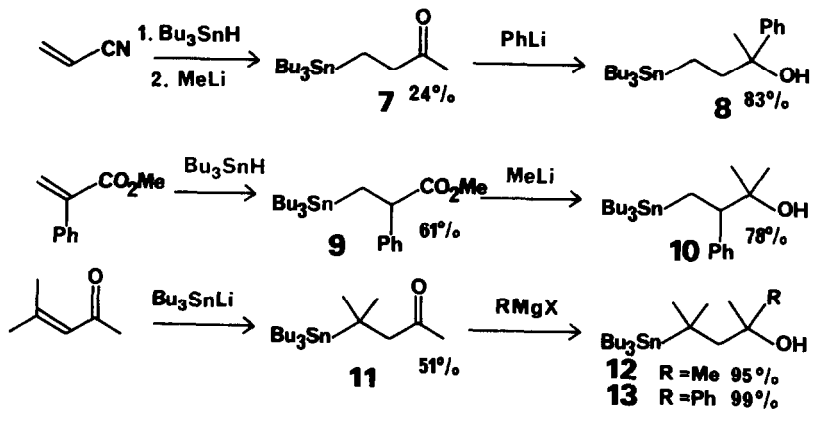
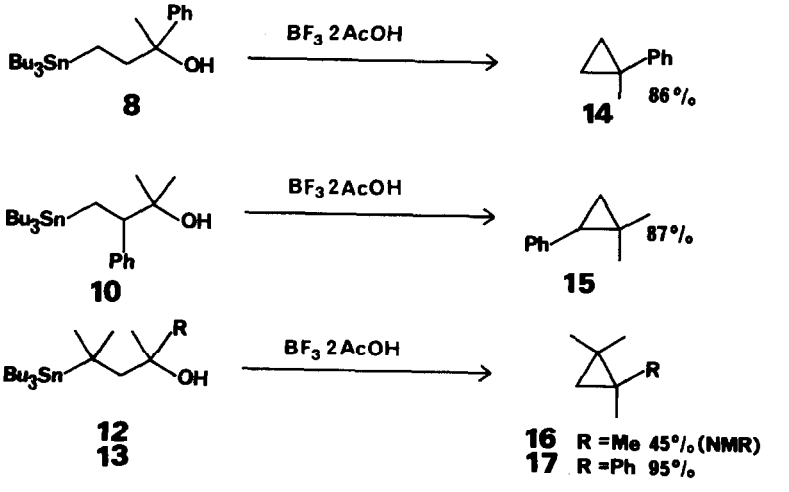
SCHEME 1




SCHEME 2



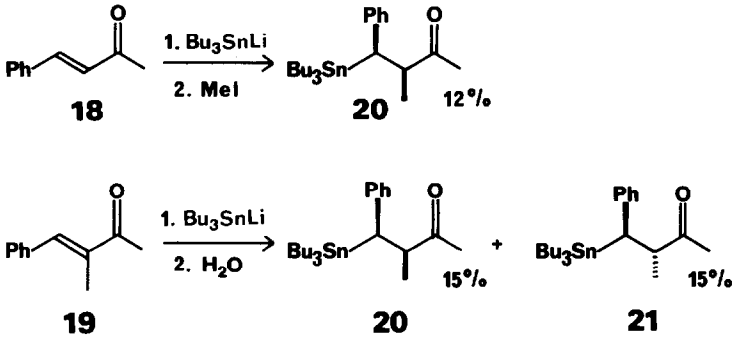

SCHEME 3



alcohol **10**), rearrangement is not competitive with cyclopropane formation. Secondly, it shows that cyclopropane formation occurs in high yield even if two fully-substituted centres are being brought together, as with cyclopropanes **16** and **17**.

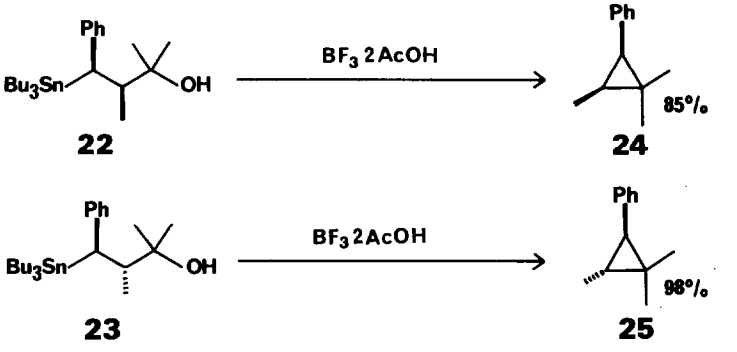
Having established that the reaction goes in good yield even under fairly demanding circumstances, we next investigated the stereochemistry. Conjugate addition of trialkyltin-lithium to the enones **18** and **19**, followed by quenching the intermediate enolates with methyl iodide and water respectively, gave the ketones **20** and **21**. To discover if the reaction was stereospecific at the tin-bearing carbon atom, we prepared the two alcohols **22** and **23** from these ketones. Treatment of these alcohols with acid gave the cyclopropanes **24** and **25**, respectively, in high yield. Having shown that the reaction was stereospecific at the tin-bearing carbon atom,

SCHEME 4




our next step was to discover if it could be stereospecific at the hydroxyl-bearing carbon atom. We used the two alcohols **27** and **28**, as shown in Scheme 6. The

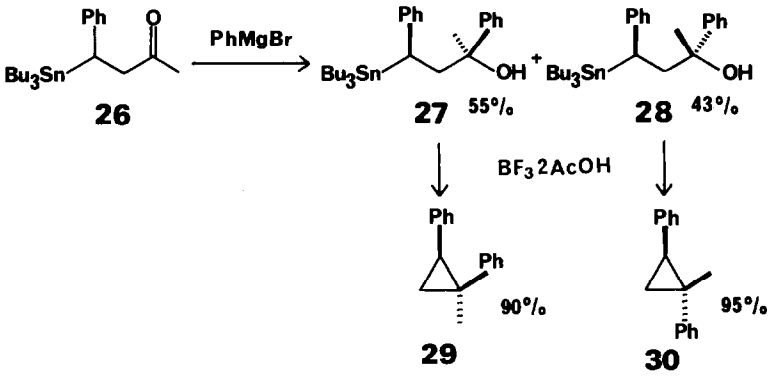
SCHEME 5




stereospecificity at the hydroxyl-bearing carbon atom is remarkable in view of its tertiary benzylic nature.

Although we had now shown that the reaction was stereospecific, we did not yet know that it went with inversion of configuration at both centres (as illustrated). We proved this with the following example. Conjugate addition of trimethyltin-lithium to the enone **18**, followed by methylation of the intermediate enolate, gave the

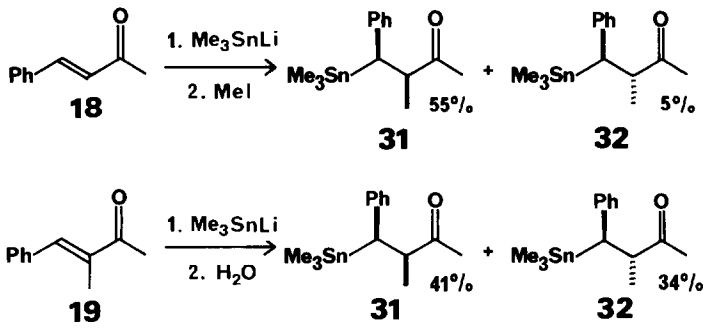
SCHEME 6




ketones **31** and **32** with high diastereoselectivity. The diastereoselectivity of these conjugate addition-alkylation reactions (Scheme 7) is a general feature, and allowed us to synthesise selectively several stereochemically defined alcohols. The sense of the diastereoselectivity was deduced at first by analogy with several similarly diastereoselective reactions in the silicon series [9], but was confirmed by the X-ray crystal structure described below.

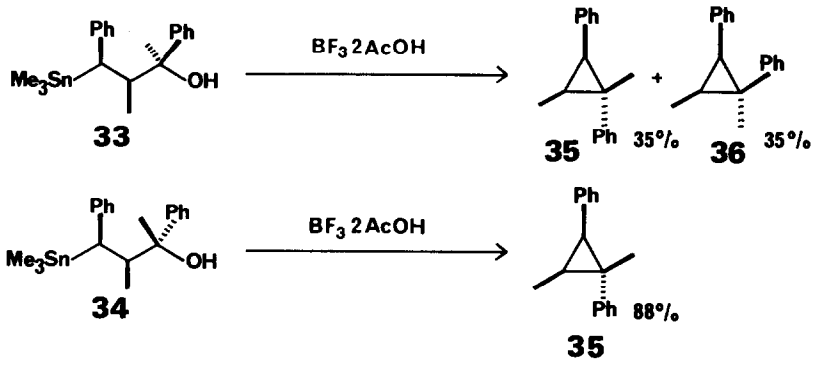
Treatment of the major ketone **31** with the phenyl Grignard reagent gave the alcohols **33** and **34**, also with high diastereoselectivity, although curiously in an anti-Cram sense. Proof of the structure was provided by an X-ray crystal structure determination [10] on the major alcohol **33**. When we treated the alcohol **34** with acid, we obtained only one cyclopropane **35**. However, the alcohol **33** gave a mixture of cyclopropanes **35** and **36** (Scheme 8). This is not too surprising, since inversion of

SCHEME 7



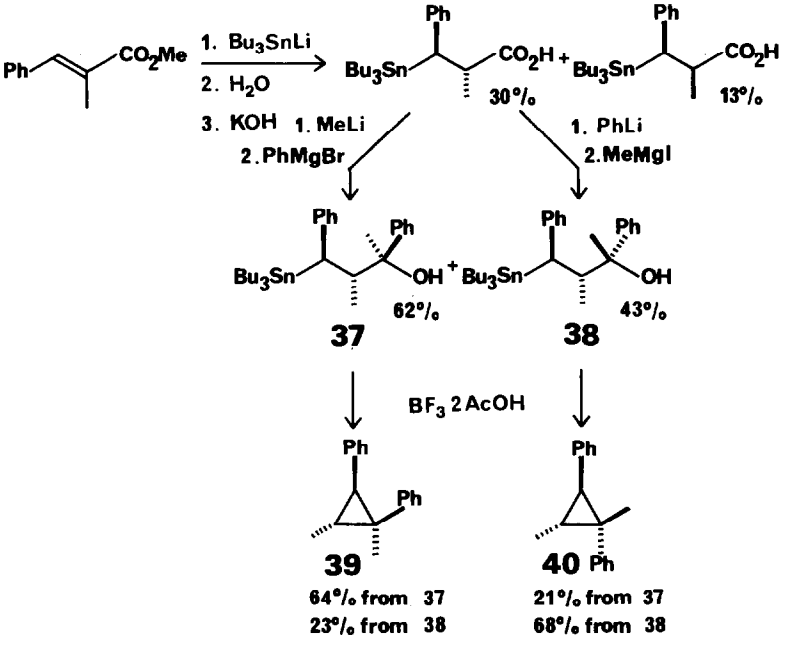

configuration at both centres of this isomer would make the sterically more crowded cyclopropane **36**. The surprise is that a tertiary benzyl alcohol should show even this amount of stereospecificity. All our other stereochemical assignments were made by analogy with this pair of compounds, working back from the stereochemistry of the cyclopropanes produced.

SCHEME 8




That the reaction can be adapted to produced other cyclopropanes stereospecifically is shown by the sequence in Scheme 9. Taking advantage of the stereocontrol of the conjugate addition reaction and (this time) the usual Cram selectivity of addition to the intermediate ketones, we made the alcohols **37** and **38**. This is an alternative preparation of the ketone **21**. The usual acid conditions, converted the alcohols **37** and **38** into the cyclopropanes **39** and **40** with high, but not complete, stereospecificity.

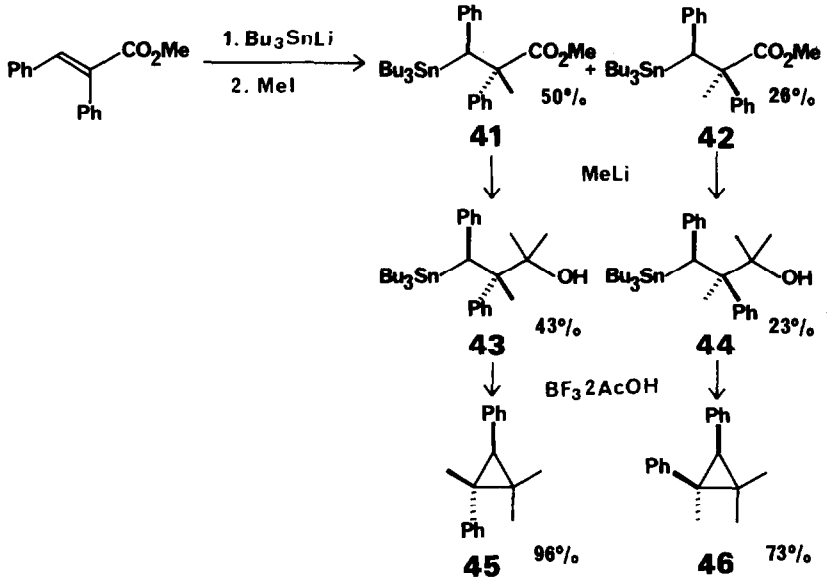
SCHEME 9




In none of the examples so far did we see rearrangement, as we had with the corresponding silicon compounds [2]. To examine whether this could be competitive under the most favourable conditions, we made the alcohols **43** and **44**. These

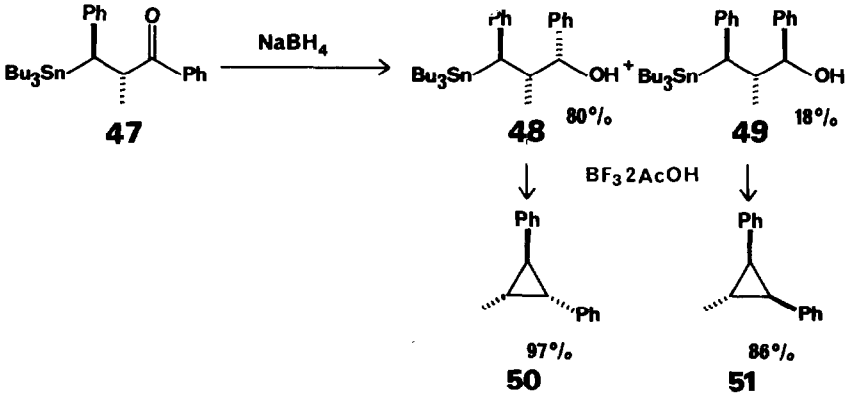
alcohols are such that a phenyl group (a good migrator) could migrate, leaving a tertiary carbonium ion. Scheme 10 shows that, once again, the cyclopropanes **45** and **46** were formed with no trace of rearrangement. Thus, as rearrangement is not competitive under these most favourable conditions, it is unlikely ever to be a major reaction pathway.

SCHEME 10



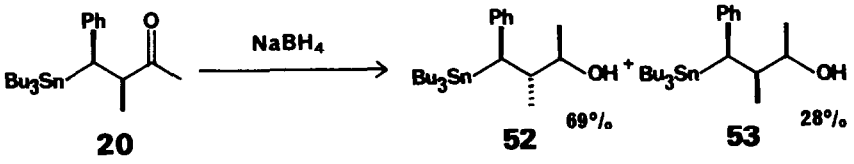

So far we had only looked at tertiary alcohols. We found that the reaction also works well with secondary benzylic alcohols **48** and **49** (Scheme 11), but with secondary alkyl alcohols **52** and **53** decomposition occurred without cyclopropane formation (Scheme 12).

SCHEME 11




The structures of the cyclopropanes produced were easily assigned by $^1$H NMR spectroscopy. In particular, the *cis*-vicinal coupling constants fell in the range 8–11

SCHEME 12




20 52 53

Hz and the *trans* in the range 5–8 Hz. The presence of phenyl groups was a further help, since the chemical shift of a methyl group on a cyclopropane with a *cis* phenyl group is about 0.4 ppm upfield from one with a *trans* phenyl group [11].

That the cyclopropanes were produced with inversion of configuration at both centres (via a "W" conformation) had some hint of precedent in the work of Davis [4]. Working with conformationally locked γ-mesyloxy stannanes he found that only the one in the "W" conformation reacted to form a cyclopropane. Further precedent was provided by work with analogous boron compounds, where inversion of configuration at the boron-bearing carbon atom took place during cyclopropane formation [12].

## Conclusions

High diastereoselectivity is observed on addition of trialkyltin-lithium to α,β-unsaturated ketones and esters followed by quenching with an appropriate electrophile. The products from this reaction can be stereoselectively converted to γ-stannyl alcohols which, when treated with acid, react stereospecifically to give cyclopropanes in high yield. Taken together these reactions represent a powerful new stereoselective cyclopropane synthesis. We thank Professor C.P. Casey for spectra of the cyclopropanes **24** and **25**.

## Experimental

Melting points were measured on a Kofler hot-stage melting-point apparatus and are uncorrected. Infra-red spectra were recorded on a Perkin–Elmer 297 grating spectrophotometer and wavenumbers were measured relative to polystyrene (1603 $cm^{-1}$). Proton NMR spectra were recorded on Varian EM 360A (60 MHz), Varian EM 390 (90 MHz) or Bruker WM 250 (250 MHz) spectrometers. Chemical shifts are quoted as δ values in ppm downfield from tetramethylsilane and are measured by reference to tetramethylsilane (δ 0.00 ppm), dichloromethane (δ 5.27 ppm) or chloroform (δ 7.25 ppm) as internal standard. Mass spectra were recorded on AEI MS9 or MS30 spectrometers. For compounds containing tin the $^{120}Sn$ isotope is reported. High resolution mass spectra were recorded on an AEI MS902 spectrometer.

Flash chromatography was carried out using Kieselgel 60 (230–400 mesh). Analytical thin-layer chromatography was carried out on plates of Merck Kieselgel $60F_{254}$ and preparative thin-layer chromatography on plates coated to a thickness of 1.0 mm with Merck Kieselgel $60PF_{254}$.

*4-Trimethyltinbutan-2-one (6)*

Freshly distilled methyl vinyl ketone (**5**) (0.22 ml, 3.2 mmol) in anhydrous THF (3 ml) was added dropwise to a stirred solution of trimethyltin-lithium (2.88 mmol) in anhydrous THF (10 ml) under nitrogen at −78°C. After 10 min water was added, the mixture warmed to room temperature and extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and Kugelrohr distilled to give the ketone **6** (0.254 g, 37%, but not 100% pure), $R_F$ ($Et_2O$) 0.62, $\nu_{max}$, (film) 1714 $cm^{-1}$ (C=O), $\delta$ ($CCl_4$) 2.62 (2H, t, $J$ 7 Hz, $COCH_2$), 2.04 (3H, s, COMe), 0.76 (2H, t, $J$ 7 Hz, $SnCH_2$), and −0.01 (9H, s, $SnMe_3$), $m/z$ 221 (10%, $M$–Me), 165 (95, $SnMe_3$), 150 (24, $C_2H_6Sn$), and 135 (100, $CH_3Sn$).

*2-Methyl-4-trimethyltinbutan-2-ol (3)*

Methyllithium (1.05 ml of a 0.94 $M$ solution in ether) was added dropwise to a stirred solution of the ketone **6** (0.236 g, 1.0 mmol) in anhydrous ether (5 ml) under nitrogen at −78°C. After 5 min ethanol (1 ml) was added followed by water (2 ml), the mixture allowed to warm to room temperature and extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. Flash chromatography eluting with ether-light petroleum (5/95) gave the alcohol **3** (0.160 g, 65%), $R_F$ ($Et_2O$) 0.60, $\nu_{max}$ (film) 3370 $cm^{-1}$ (OH), $\delta$ ($CCl_4$) 1.89 (1H, s, OH), 1.7–1.4 (2H, m, $COCH_2$), 1.13 (6H, s, $CMe_2$), 0.9–0.6 (2H, m, $SnCH_2$), and 0.03 (9H, s, $SnMe_3$), $m/z$ 237 (38%, $M$ − Me), 219 (62, $M$ − (Me + $H_2O$)), 165 (100, $SnMe_3$), 149 (31, $C_2H_5Sn$), and 135 (33, SnMe).

*1,1-Dimethylcyclopropane (4)*

Boron trifluoride acetic acid complex (0.15 ml, 1.1 mmol) was added to a stirred solution of the alcohol **3** (0.277 g, 1.10 mmol) in anhydrous dichloromethane (0.5 ml) under nitrogen at 0°C. After 15 min the reaction was allowed to warm to room temperature and dry nitrogen was passed through the reaction, then through a potassium hydroxide tube and condensed at −78°C to give the cyclopropane **4** [13] (only, by NMR), $\delta$ ($CCl_4$) 0.99 (6H, s, $Me_2$), and 0.17 (4H, s, $C_2H_4$).

*2-Tributyltin ethylcyanide*

This was prepared by the method of Van der Kerk [8]. Tributyltin hydride (2.65 ml, 10 mmol) and acrylonitrile (1.32 ml, 20 mmol) were heated at 80°C for 4 h. Evaporation in vacuo followed by flash chromatography eluting with ether-light petroleum (5/95) gave the nitrile (1.38 g, 40%), $R_F$ ($Et_2O$) 0.78, $\nu_{max}$ (film) 2400 $cm^{-1}$ (CN), $\delta$ ($CCl_4$) 2.36 (2H, t, $J$ 8 Hz, $CH_2CN$) and 1.5–0.4 (29H, m, $CH_2SnBu_3$), $m/z$ 345 (6%, $M^+$), 288 (10, $M$ − Bu), 235 (17, $C_8H_{19}Sn$), 232 (63, $C_7H_{14}NSn$), 177 (33, $C_4H_9Sn$), 176 (29, $C_3H_6NSn$), 135 (9, $CH_3Sn$), and 121 (27, HSn).

*4-Tributyltinbutan-2-one (7)*

This was prepared by the method of Van Leusen [14]. Methyllithium (8.0 ml of a 1.0 $M$ solution in ether) was added to a stirred solution of the nitrile (1.38 g, 4 mmol) in anhydrous ether (10 ml) under nitrogen at 5°C. After 30 min at room temperature, water (5 ml) was slowly added. The organic layer was separated, evaporated in vacuo, acetone (5 ml) and 6$N$ hydrochloric acid (5 ml) added, and the mixture refluxed for 15 min. The mixture was then neutralized with 10% sodium

hydroxide, and extracted with ether. The combined extracts were dried ($MgSO_4$) and flash chromatographed eluting with ether-light petroleum (5/95), to give the ketone **7** (0.852 g, 59%), $R_F$ ($Et_2O$) 0.65, $\nu_{max}$ (film) 1711 $cm^{-1}$ (C=O), $\delta$ ($CCl_4$) 2.59 (2H, t, $J$ 7.5 Hz, $COCH_2$), 2.03 (3H, s, Me), and 2.0–0.5 (29H, m, $CH_2SnBu_3$), $m/z$ 305 (100%, Sn-Bu), 249 (11, $C_8H_{17}OSn$), 191 (18, $C_5H_{11}Sn$), 177 (13, $C_4H_9Sn$), and 121 (4, HSn).

*2-Phenyl-4-tributyltinbutan-2-ol (**8**)*

Phenyllithium (3.8 ml of a 1.05 $M$ solution in ether) was added dropwise to a stirred solution of the ketone **7** (0.722 g, 2 mmol) in anhydrous ether (10 ml) under nitrogen at 0°C. After 15 min water (5 ml) was slowly added, the mixture extracted with ether and the combined extracts dried ($MgSO_4$) and evaporated in vacuo. Flash chromatography eluting with ether-light petroleum (5/95) gave the alcohol **8** (0.731 g, 83%), $R_F$ ($Et_2O$) 0.76, $\nu_{max}$ (film) 3440 (OH) and 1602 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–7.1 (5H, m, Ph), 1.49 (3H, s, Me) and 2.0–0.4 (32H, m, remaining H's), $m/z$ 412 (1%, $M - C_2H_4$), 383 (43, $M$ – Bu), 365 (100, $M - (Bu + H_2O)$), 354 (2, $M - C_6H_{14}$), 291 (33, $M - C_{11}H_{17}$), 269 (5, $M - C_{12}H_{27}$), 251 (62, $M - C_{12}H_{29}O$), 235 (13, $C_8H_{19}Sn$), and 177 (27, $C_4H_9Sn$).

*Methyl 2-Phenyl-3-tributyltinpropanate (**9**)*

This was prepared by the method of Van der Kerk [8]. Tributyltin hydride (1.33 ml, 5 mmol) and methyl 2-phenylacrylate (0.810 g, 5 mmol) were heated at 80°C for 4.5 h. Flash chromatography eluting with ether-light petroleum (5/95) gave the ester **9** (1.380 g, 61%), $R_F$ ($Et_2O$) 0.75, $\nu_{max}$ (film) 1741 (C=O) and 1601 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.4–7.2 (5H, m, Ph), 3.73 (1H, t, $J$ 9 Hz, PhCH), 3.64 (3H, s, OMe) and 1.8–0.4 (29H, m, $CH_2SnBu_3$), $m/z$ 397 (100%, $M$ – Bu), 341 (1, $M - C_8H_{17}$), 291 (2, $SnBu_3$), 283 (6, $M - C_{12}H_{27}$), 265 (2, $C_8H_{17}O_2Sn$), 235 (2, $C_8H_{19}Sn$), 177 (9, $C_4H_9Sn$), 151 (20, $CH_3OSn$), 121 (7, HSn), 91 (1, $C_7H_7$), and 77 (3, Ph).

*2-Methyl-3-phenyl-4-tributyltinbutan-2-ol (**10**)*

Methyllithium (8.0 ml of a 1.0 $M$ solution in ether) was added dropwise to a stirred solution of the ester **9** (1.21 g, 2.67 mmol) in anhydrous ether (20 ml) under nitrogen at −78°C. After 1 h methanol (1 ml) was added followed by water (5 ml). The mixture was warmed to room temperature and extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and flash chromatographed eluting with ether-light petroleum (10/90) to give the alcohol **10** (0.946 g, 78%), $R_F$ ($Et_2O$) 0.71, $\nu_{max}$ (film) 3450 (OH) and 1492 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.24 (5H, br s, Ph), 2.76 (1H, dd, $J$ 9 and 7 Hz, PhCH), and 1.5–0.4 (36H, m, remaining H's), $m/z$ 439 (0.5%, $M$ – Me), 397 (52, $M$ – Bu), 379 (30, $M - C_4H_{11}O$), 291 (47, $C_{12}H_{28}Sn$), 251 (100, $C_9H_{23}Sn$), 235 (22, $C_8H_{19}Sn$), 177 (38, $C_4H_9Sn$), 137 (13, SnOH), 121 (18, HSn), and 91 (8, $C_7H_7$).

*4-Methyl-4-tributyltinpentan-2-one (**11**)*

Mesityl oxide (0.49 g, 5 mmol) in anhydrous THF (5 ml) was added dropwise to a stirred solution of tributyltin-lithium (5.4 mmol) in HMPA (1 ml) and THF (10 ml) under nitrogen at −78°C. After 5 min ethanol (1 ml) was added followed by saturated ammonium chloride (5 ml) and the mixture warmed to room temperature. The organic layer was separated, repeatedly washed with water, dried ($MgSO_4$), and

evaporated in vacuo. Flash chromatography eluting with ether-light petroleum (5/95) gave the ketone **11** (0.985 g, 51%), $R_F$ ($Et_2O$) 0.74, $\nu_{max}$ (film) 1718 $cm^{-1}$ (C=O), $\delta$ ($CCl_4$) 2.39 (2H, s, $COCH_2$), 2.02 (3H, s, COMe), 1.03 (6H, s, $Me_2$), and 1.8–0.5 (27H, m, $SnBu_3$), *m/z* 390 (0.05%, $M^+$), 347 (0.05, $M - Ac$), 333 (100, $M - Bu$), 291 (5, $SnBu_3$), 277 (2, $M - C_8H_{12}$), 235 (7, $C_8H_{19}Sn$), 219 (3, $M - C_{12}H_{27}$), 177 (7, $C_4H_9Sn$), 137 (2, SnOH), and 121 (6, HSn).

*2,4-Dimethyl-4-tributyltinpentan-2-ol (12)*

Methyl magnesium iodide (2.0 ml of a 1.0 *M* solution in ether) was added dropwise to a stirred solution of the ketone **11** (0.484 g, 1.24 mmol) in anhydrous ether (5 ml) under nitrogen at 0°C. After 1 h water was cautiously added and the mixture extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and flash chromatographed eluting with ether-light petroleum to give the alcohol **12** (0.475 g, 95%), $R_F$ ($Et_2O$) 0.74, $\nu_{max}$ (film) 3620 and 3470 (br) $cm^{-1}$ (OH), $\delta$ ($CCl_4$) 1.03 (6H, s, $Me_2$), 0.95 (6H, s, $Me_2$) and 1.6–0.6 (30H, m, remaining H's), *m/z* 406 (0.005%, $M^+$), 349 (10, $M - Bu$), 331 (50, $M - (Bu + H_2O)$), 291 (60, $C_{12}H_{28}Sn$), 251 (40, $M - C_{10}H_{19}O$), 235 (54, $C_8H_{19}Sn$), 177 (71, $C_4H_9Sn$), 137 (21, SnOH), and 121 (21, HSn).

*4-Methyl-2-phenyl-4-tributyltinpentan-2-ol (13)*

Phenyl magnesium bromide (2.0 ml of a 1.0 *M* solution in ether) was added dropwise to a stirred solution of the ketone **11** (0.430 g, 1.10 mmol) in anhydrous ether (5 ml) under nitrogen at 0°C. After 1 h the same work up as used for alcohol (**12**) was followed to give the alcohol (**13**) (0.513 g, 99%), $R_F$ ($Et_2O$) 0.77, $\nu_{max}$ (film) 3600 (OH) and 1600 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–7.1 (5H, m, Ph), 1.97 (1H, s, OH), and 1.7–0.4 (35H, m, remaining H's), *m/z* 468 (21%, $M^+$), 450 (7, $M - H_2O$), 411 (71, $M - Bu$), 393 (100, $M - (Bu + H_2O)$), 291 (64, $SnBu_3$), and 177 (36, $C_4H_9Sn$).

*1-Methyl-1-phenylcyclopropane (14)*

Boron trifluoride acetic acid complex (0.14 ml, 1 mmol) was added to a stirred solution of the alcohol **8** (0.439 g, 1 mmol) in anhydrous dichloromethane (2 ml) under nitrogen at 0°C. After 14 min 10% sodium hydroxide solution (2 ml) was added, the organic layer was separated, dried ($MgSO_4$), evaporated in vacuo (20 mmHg), and Kugelrohr distilled (oven temperature 160°C/20 mmHg) to give the cyclopropane **14** [15] (0.114 g, 86%), $R_F$ (pentane) 0.45, $\nu_{max}$ (film) 1603, 1578 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–7.2 (5H, m, Ph), 1.62 (3H, s, Me), and 1.2–0.8 (4H, m, $C_3H_4$) (Found: $M^+$, 132.0937. $C_{10}H_{12}$ calcd.: 132.0939), *m/z* 132 (41%, $M^+$), 131 (28, $M - H$), 117 (100, $M - Me$), 103 (6, $M - C_2H_5$), 91 (18, $C_7H_7$), and 77 (11, Ph).

*1,1-Dimethyl-2-phenylcyclopropane (15)*

This was prepared by the same method as cyclopropane **14** using alcohol **10** (0.453 g, 1.0 mmol) to give the cyclopropane **15** [16] (0.127 g, 87%), $R_F$ (pentane) 0.49, $\nu_{max.}$ ($CCl_4$) 1604 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–7.2 (5H, m, Ph), 2.0–1 (1H, dd, *J* 8 and 6 Hz, PhCH), 1.38 (3H, s, Me), 0.95 (3H, s, Me), and 1.0–0.8 (2H, m, $CH_2$) (Found: $M^+$, 146.1097. $C_{11}H_{14}$ calcd. 146.1096), *m/z* 146 (9%, $M^+$), 132 (36, $M - CH_2$), 131 (52, $M - Me$), 117 (100, $M - C_2H_5$), and 91 (38, $C_7H_7$).

*1,1,2,2-Tetramethylcyclopropane (16)*

Boron trifluoride acetic acid complex (0.13 ml, 0.94 mmol) was added to a stirred solution of the alcohol **12** (0.380 g, 0.94 mmol) in deuterodichloromethane (1 ml) under nitrogen at 0°C. After 15 min 10% sodium hydroxide solution (3 ml) was added. The organic layer was separated, dried ($MgSO_4$), and Kugelrohr distilled (oven temperature 140°C) to give the cyclopropane **16** (45% by NMR), $\delta$ ($CD_2Cl_2$) 1.07 (12H, s, Me) and 0.10 (2H, s, $C_3H_2$) (Found: $M^+$, 98.1095. $C_7H_{14}$ calcd. 98.1095), *m/z* 98 (10%, $M^+$), 83 (20, $M-Me$) and 55 (15, $C_4H_7$).

*1-Phenyl-1,2,2-trimethylcyclopropane (17)*

This was prepared by the same method as cyclopropane **14** using alchol **13** (0.370 g, 0.792 mmol) to give the cyclopropane **17** [17] (0.120 g, 95%), $R_F$ (pentane) 0.45, $\nu_{max}$ ($CCl_4$) 1602 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–7.1 (5H, m, Ph), 1.39 (3H, s, Me), 1.27 (3H, s, Me), 0.89 (1H, d, *J* 4.5 Hz, $C_3H_AH_B$), 0.73 (3H, s, Me), and 0.45 (1H, d, *J* 4.5 Hz, $C_3H_AH_B$) (Found: $M^+$, 160.1251. $C_{12}H_{16}$ calcd. 160.1252), *m/z* 160 (33%, $M^+$), 145 (100, $M-Me$), 117 (24, $M-C_3H_7$), 105 (15, $M-C_4H_7$), 23 (24, $C_7H_7$), 23 (24, $C_7H_7$), and 77 (15, Ph).

*(3RS,4RS)-3-Methyl-4-phenyl-4-tributyltinbutan-2-one (20)*

The enone **18** (1.46 g, 10 mmol) in anhydrous THF (10 ml) was added dropwise to a stirred solution of tributyltin-lithium (10 mmol) in anhydrous THF (30 ml) under nitrogen at −78°C. After 5 min iodomethane (0.62 ml, 10 mmol) was added, the mixture warmed to room temperature, water added, and the mixture extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and flash chromatographed eluting with ether-light petroleum (5/95) to give the ketone **20** (0.535 g, 12%), $R_F$ ($Et_2O$) 0.77, $\nu_{max}$ (film) 1717 (C=O) 1601 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–6.9 (5H, m, Ph), 3.26 (1H, dq, *J* 9 and 7 Hz, COCH), 2.58 (1H, d, *J* 9 Hz, PhCH), 2.26 (3H, s, COMe), 1.13 (3H, d, *J* 7 Hz, Me), and 1.5–0.6 (27H, m, $SnBu_3$), *m/z* 452 (0.2%, $M^+$, 451 (2, $M-H$), 409 (14, $M-Ac$), 395 (100, $M-Bu$), 361 (14, $M-C_7H_7$), 343 (29, $M-C_7H_9$)), 291 (12, $SnBu_3$), 251 (20, $Bu_2SnOH$), 235 (49, $C_8H_{19}Sn$), 179 (67, $C_4H_{11}Sn$), 137 (18, SnOH, and 121 (24, HSn).

*3-Methyl-4-phenyl-4-tributyltinbutan-2-one (20) and (21)*

These were prepared by the same method as ketone **20** using enone **19** (1.60 g, 10 mmol) and quenching with methanol (1 ml) followed by water (5 ml) to give the (3*RS*, 4*RS*)-ketone **20** (0.656 g, 15%) and the (3*RS*,4*SR*)-ketone **21** (0.591 g, 13%), $R_F$ ($Et_2O$) 0.70, $\nu_{max}$ (film) 1710 (C=O) and 1594 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–6.9 (5H, m, Ph), 3.23 (1H, dq, *J* 12 and 7 Hz, COCH), 2.73 (1H, d, *J* 12 Hz, PhCH), 1.85 (3H, s, COMe), 1.20 (3H, d, *J* 7 Hz, Me), and 1.5–0.6 (27, H, m, $SnBu_3$), *m/z* 452 (0.01%, $M^+$), 451 (0.01, $M-H$), 395 (92, $M-Bu$), 291 (22, $SnBu_3$), 281 (7, $M-3Bu$), 235 (46, $C_8H_{19}Sn$), 179 (100, $C_4H_{11}Sn$), 137 (15, SnOH), and 121 (51, HSn).

*(3RS,4RS)-2,3-Dimethyl-4-phenyl-4-tributyltinbutan-2-ol (22)*

This was prepared by the same method as alcohol **12** using ketone **20** (0.255 g, 0.565 mmol) to give the alcohol **22** (0.240 g, 91%), $R_F$ ($Et_2O$) 0.74, $\nu_{max.}$ (film) 3600 and 3450 (br) (OH) and 1597 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–6.9 (5H, m, Ph), 2.45 (1H, d, *J* 10 Hz, PhCH), 2.23 (1H, dq, *J* 10 and 7 Hz, MeC*H*), 1.30 (3H, s,

Me), 1.16 (3H, s, Me), and 1.5–0.5 (31H, m, remaining H's), *m/z* 467 (1%, $M - H$), 450 (0.5, $M - H_2O$), 411 (55, $M - Bu$), 393 (40, $M - (Bu + H_2O)$), 291 (40, $SnBu_3$), 251 (10, $Bu_2SnOH$), 235 (35, $C_8H_{19}Sn$), 177 (80, $C_4H_9Sn$), 137 (50, SnOH), and 121 (26, HSn).

*(3RS,4SR)-2,3-Dimethyl-4-phenyl-4-tributyltinbutan-2-ol (23)*

This was prepared by the same method as alcohol **12** using ketone **21** (0.156 g, 0.346 mmol) to give the alcohol **23** (0.145 g, 90%), $R_F$ ($Et_2O$) 0.68, $\nu_{max}$ (film) 3600 and 3450 (br) (OH) and 1600 and 1497 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–6.9 (5H, m, Ph), 2.71 (1H, d, *J* 10.5 Hz, PhCH), 2.46 (1H, dq, *J* 10.5 and 7 Hz, MeC*H*), 1.13 (3H, s, Me), 1.06 (3H, s, Me), and 1.4–0.6 (31H, m, remaining H's), *m/z* 467 (0.2%, $M - H$), 450 (0.2, $M - H_2O$), 411 (35, $M - Bu$), 393 (7, $M - (Bu + H_2O)$), 291 (52, $SnBu_3$), 251 (27, $Bu_2SnOH$), 235 (35, $C_8H_{19}Sn$), 177 (100, $C_4H_9Sn$), 137 (31, SnOH), and 121 (67, HSn).

*cis-1,1,3-Trimethyl-2-phenylcyclopropane (24)*

This was prepared by the same method as cyclopropane **14** using alcohol **22** (0.164 g, 0.350 mmol) to give the cyclopropane **24** [16] (0.050 g, 89%), $R_F$ (pentane) 0.43, $\nu_{max}$ ($CCl_4$) 1602 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_3$) 7.4–7.2 (5H, m, Ph), 1.84–1.78 (1H, m, PhCH), 1.26 (3H, s, Me *trans* to Ph), 0.95 (3H, s, Me), and 0.99–0.92 (4H, m, remaining H's) (Found: $M^+$, 160.1258. $C_{12}H_{16}$ calcd. 160.1252), *m/z* 160 (53%, $M^+$), 145 (10, $M - Me$), 130 (10, $M - 2Me$), 117 (18, $M - C_3H_7$), 105 (8, $M - C_4H_9$), 91 (28, $C_7H_7$), 77 (10, Ph), and 68 (20, $C_5H_8$).

*trans-1,1,3-Trimethyl-2-phenylcyclopropane (25)*

This was prepared by the same method as cyclopropane **14** using alcohol **23** (0.145 g, 0.310 mmol) to give the cyclopropane **25** [16] (0.049 g, 98%), $R_F$ (pentane) 0.43, $\nu_{max}$ ($CCl_4$) 1602 and 1493 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–7.1 (5H, m, Ph), 1.50 (1H, d, *J* 5.5 Hz, PhCH), 1.23 (3H, d, *J* 5.5 Hz, Me), 1.22 (3H, s, Me), 1.10 (1H, quin, *J* 5.5 Hz, MeC*H*), and 0.83 (3H, s, Me *cis* to Ph) (Found: $M^+$, 160.1249. $C_{12}H_{16}$ calcd. *M*, 160. 1252), *m/z* 160 (35%, $M^+$), 145 (100, $M - Me$), 130 (11, $M - 2Me$), 117 (31, $M - C_3H_7$), 105 (12, $M - C_4H_9$), and 91 (44, $C_7H_7$).

*4-Phenyl-4-tributyltinbutan-2-one (26)*

The enone **18** (1.460 g, 10 mmol) in anhydrous THF (10 ml) was added dropwise over 5 min to a stirred solution of tributyltin-lithium (10 mmol) in anhydrous THF (30 ml) under nitrogen at −100°C. After 5 min the same work-up as for ketone **20** was followed to give the ketone **26** (0.806 g, 18%), $R_F$ ($Et_2O$) 0.75, $\nu_{max}$ (film) 1718 (C=O) and 1601 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.2–2.7 (3H, m, $COCH_2$ and PhCH), 2.09 (3H, s, COMe), and 1.8–0.3 (27H, m, $SnBu_3$), *M/z* 438 (0.01%, $M^+$), 381 (100, $M - Bu$), 350 (1, $M - C_5H_{12}O$), 323 (1, $M - C_8H_{19}$), 291 (13, $SnBu_3$), 267 (13, $M - C_{12}H_{27}$), 235 (31, $C_8H_{19}Sn$), 197 (5, $C_6H_5Sn$), 177 (40, $C_4H_9Sn$), and 121 (13, HSn).

*2,4-Diphenyl-4-tributyltinbutan-2-ol (27) and (28)*

These were prepared by the same method as alcohol **13** using ketone **26** (0.690 g, 1.58 mmol) and phenyl magnesium bromide (3 ml of a 1.0 *M* solution in ether) to give (2*RS*, 4*SR*)-alcohol (**27**) (0.446 g, 55%), $R_F$ ($Et_2O$) 0.77, $\nu_{max.}$ (film) 3570 and

3450 (br) (OH) and 1601 and 1491 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–6.9 (10H, m, 2 × Ph), 2.9–2.3 (3H, m, $PhCHCH_2$), 1.88 (1H, s, OH), 1.52 (3H, s, Me) and 1.7–0.4 (27H, m, $SnBu_3$), *m/z* 516 (1%, $M^+$), 459 (10, $M - Bu$), 441 (7, $M - (Bu + H_2O)$), 357 (22, $M - C_{10}H_{13}O$), 291 (40, $SnBu_3$), 251 (60, $Bu_2SnOH$), 235 (19, $C_8H_{19}Sn$), 208 (100, $C_{16}H_{16}$), and 121 (67, HSn), and (2*RS*, 4*RS*)-alcohol **28** (0.346 g, 43%), $R_F$ ($Et_2O$) 0.74, $\nu_{max}$ (film) 3410 (br) (OH) and 1601 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–6.9 (10H, m, 2 × Ph), 2.9–2.3 (3H, m, $PhCHCH_2$), 1.98 (1H, s, OH, 1.49 (3H, s, Me) and 1.8–0.4 (27H, m, $SnBu_3$), *m/z* 516 (1%, $M^+$), 459 (6, $M - Bu$), 441 (7, $M - (Bu + H_2O)$), 357 (6, $M - C_{10}H_{23}O$), 291 (26, $SnBu_3$), 251 (20, $Bu_2SnOH$), 235 (13, $C_8H_{19}Sn$), 208 (100, $C_{16}H_{16}$), and 121 (50, HSn).

*cis-1,2-Diphenyl-1-methylcyclopropane (29)*

This was prepared by the same method as cyclopropane **14** using alcohol **27** (0.343 g, 0.666 mmol) but instead of being distilled the crude product was purified by preparative thin-layer chromatography eluting with ether-light petroleum (1/99) to give the cyclopropane **29** [18] (0.124 g, 90%) as needles, m.p. 35–36°C (from light petroleum), $R_F$ (pentane) 0.18, $\nu_{max}$ ($CCl_4$) 1603 and 1499 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.2–7.0 (8H, m, Ph), 6.8–6.7 (2H, m, Ph), 2.23 (1H, dd, *J* 8.5 and 6 Hz, PhCH), 1.55 (3H, s, Me), 1.51 (1H, dd, *J* 6 and 5.5 Hz, $CH_AH_B$) and 1.27 (1H, dd, *J* 8.5 and 5.5 Hz, $CH_AH_B$), (Found: $M^+$, 208.1245. $C_{16}H_{16}$ calcd. 208.1252), *m/z* 208 (100%, $M^+$), 193 (82, $M - Me$), 178 (22, $M - C_2H_6$), 130 (24, $M - C_6H_6$), 129 (20, $M - C_6H_7$), 115 (100, $M - C_7H_9$), and 91 (48, $C_7H_7$).

*trans-1,2-Diphenyl-1-methylcyclopropane (30)*

This was prepared by the same method as cyclopropane **29** using alcohol **28** (0.268 g, 0.520 mmol) to give the cyclopropane **30** [18] (0.102 g, 95%), $R_F$ (pentane) 0.15, $\nu_{max}$ ($CCl_4$) 1604 and 1500 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.4–7.2 (10H, m, 2 × Ph), 2.44 (1H, dd, *J* 9 and 6.5 Hz, PhCH), 1.47 (1H, dd, *J* 9 and 5 Hz, $CH_AH_B$), 1.27 (1H, dd, *J* 6.5 and 5 Hz, $CH_AH_B$), and 1.15 (3H, s, Me) (Found: $M^+$, 208.1257. $C_{16}H_{16}$ calcd. 208.1252), *m/z* 208 (100%, $M^+$), 193 (41, $M - Me$), 178 (16, $M - C_2H_6$), 130 (25, $M - C_6H_6$), 129 (20, $M - C_6H_7$), 115 (84, $M - C_7H_9$), and 92 (17, $C_7H_7$).

*3-Methyl-4-phenyl-4-trimethyltinbutan-2-one (31) and (32)*

These were prepared by the same method as ketone **20** using enone **18** (0.657 g, 4.5 mmol) to give (3*RS*,4*RS*)-ketone **31** (0.810 g, 55%), $R_F$ ($Et_2O$) 0.75, $\nu_{max}$ (film) 1717 (C=O) and 1600 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.20 (1H, br quin, *J* 8 Hz, COCH), 2.43 (1H, d, *J* 8.5 Hz, PhCH), 2.21 (3H, s, COMe), 1.14 (3H, d, *J* 7 Hz, Me), and −0.08 (9H, s, $SnMe_3$), *m/z* 326 (2%, $M^+$), 311 (75, $M - Me$), 281 (4, $M - C_3H_9$), 253 (4, $M - C_4H_9O$), 165 (100, $SnMe_3$), 150 (12, $C_2H_6Sn$), and 135 (39, $CH_3Sn$), and (3*RS*,4*SR*)-ketone (**32**) (0.067 g, 5%), $R_F$ ($Et_2O$) 0.74, $\nu_{max}$ (film) 1711 (C=O) and 1598 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.42 (1H, dq, *J* 11 and 7 Hz, COCH), 2.66 (1H, d, *J* 11 Hz, PhCH), 1.80 (3H, s, COMe), 1.15 (3H, d, *J* 7 Hz, Me), and −0.03 (9H, s, $SnMe_3$), *m/z* 326 (2%, $M^+$), 311 (55, $M - Me$), 281 (3, $M - C_3H_9$), 253 (3, $M - C_4H_9O$), 165 (100, $SnMe_3$), 150 (12, $C_2H_6Sn$), and 135 (31, $CH_3Sn$).

*2,4-Diphenyl-3-methyl-4-trimethyltinbutan-2-ol (33) and (34)*

These were prepared by the same method as alcohol **13** using ketone **31** (0.720 g, 2.21 mmol) and stirring for 2 h to give (2*RS*,3*SR*,4*SR*)-alcohol **33** (0.698 g, 79%) as prisms, m.p. 98–99°C (from methanol/water) (Found: C, 59.4; H, 6.90. $C_{20}H_{28}OSn$ calcd.: C, 59.6; H, 7.00%), $R_F$ ($Et_2O$) 0.78, $\nu_{max}$ ($CCl_4$) 3600 (OH) and 1601 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–6.8 (10H, m, Ph), 2.49 (1H, dq, *J* 11.5 and 6 Hz, COCH), 2.31 (1H, d, *J* 11.5 Hz, PhCH), 1.65 (1H, s, OH), 1.53 (3H, s, Me), 0.52 (3H, d, 6 Hz, Me) and −0.13 (9H, s, $SnMe_3$), *m/z* 404 (0.1%, $M^+$), 389 (1, $M$ − Me), 371 (4, $M$ − (Me + $H_2O$)), 255 (1, $C_{10}H_{15}Sn$) 222 (69, $C_{17}H_{18}$), 208 (100, $C_{16}H_{16}$), 165 (48, $SnMe_3$), and 135 (19, $CH_3Sn$), and (2*RS*,3*RS*,4*RS*)-alcohol **34** (0.063 g, 7%) as prisms, m.p. 92.5–93°C (from methanol/water) (Found: C, 59.7; H, 6.67. $C_{20}H_{28}OSn$ calcd.: C, 59.6; H, 7.00%), $R_F$ ($Et_2O$) 0.72, $\nu_{max}$ ($CCl_4$) 3600 (OH) and 1599 and 1489 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–6.8 (10H, m, Ph), 2.8–2.3 (2H, m, PhCHCH), 2.16 (1H, s, OH), 1.63 (3H, s, Me), 0.77 (3H, d, *J* 6.5 Hz, Me), and −0.07 (9H, s, $SnMe_3$), *m/z* 404 (0.1%, $M^+$), 389 ($M$ − Me), 371 (8, $M$ − (Me + $H_2O$)), 255 (2, $C_{10}H_{15}Sn$), 222 (100, $C_{18}H_{18}$), 208 (43, $C_{16}H_{16}$), 165 (33, $SnMe_3$), and 135 (6, $CH_3Sn$).

*(1RS,2RS,3SR)- and (1RS,2SR,3RS)-1,3-Dimethyl-1,2-diphenylcyclopropane (35 and 36)*

These were prepared by the same method as cyclopropane **29** using alcohol **33** (0.130 g, 0.322 mmol) to give cyclopropanes **35** and **36** (0.050 g, 70%) in a ratio of 1/1.

*(1RS,2RS,3SR)-1,3-Dimethyl-1,2-diphenycyclopropane (35)*

This was prepared by the same method as cyclopropane **29** using alcohol **34** (0.029 g, 0.072 mmol) to give the cyclopropane **35** (0.014 g, 88%), $R_F$ (pentane) 0.17, $\nu_{max}$ ($CCl_4$) 1601 and 1497 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.5 –7.2 (10H, m, 2 × Ph), 2.46 (1H, d, *J* 9.5 Hz, PhCH), 1.60 (1H, dq, *J* 9.5 and 6.5 Hz, Me*CH*), 1.24 (3H, s, PhC*Me*), and 1.21 (3H, d, *J* 6.5 Hz, CH*Me*) (Found: $M^+$, 222.1408. $C_{17}H_{18}$ calcd. 222.1408), *m/z* 222 (79%, $M^+$), 207 (68, $M$ − Me), 193 (18, $M - C_2H_5$), 178 (20, $M - C_3H_8$), 129 (100, $M - C_7H_9$), 115 (20, $C_9H_7$), 105 (19, $C_8H_9$), and 91 (48, $C_7H_7$).

Cyclopropane **36** had: $R_F$ (pentane) 0.17, $\nu_{max.}$ ($CCl_4$) 1603 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.3–7.0 (8H, m, Ph), 6.7–6.6 (2H, m, Ph), 2.17 (1H, d, *J* 9.5 Hz, PhCH), 1.47 (3H, s, PhCMe), 1.5 (1H, m, Me*CH*), and 1.10 (3H, d, *J* 6.5 Hz, Me). For mixture with cyclopropane **35**: (Found: $M^+$, 221.1397. $C_{17}H_{18}$ calcd. 222.1408), *m/z* 222 (100%, $M^+$), 207 (52, $M$ − Me), 193 (13, $M - C_2H_5$), 178 (10, $M - C_3H_8$), 129 (52, $M - C_7H_9$), 115 (10, $C_9H_7$), 105 (10, $C_8H_9$), and 91 (32, $C_7H_7$).

*Methyl 2-methyl-3-phenyl-3-tributyltinpropanoate*

These were prepared by the same method as the mixture of ketones **20** and **21** using methyl α-methylcinnamate (0.880 g, 5 mmol) to give the (2*RS*,3*RS*)-ester (0.320 g, 14%), $R_F$ ($Et_2O$) 0.77, $\nu_{max}$ (film) 1734 (C=O) and 1600 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.69 (3H, s, OMe), 3.09 (1H, dq, *J* 11 and 7 Hz, COCH), 2.56 (1H, d, *J* 11 Hz, PhCH), 1.07 (3H, d, *J* 7 Hz, Me), and 1.6–0.4 (27H, m, $SnBu_3$), *m/z* 468 (0.5%, $M^+$), 437 (0.5, $M$ − OMe), 411 (100, $M$ − Bu), 395 (3, $M - C_4H_9O$), 383 (5, $M - C_5H_9O$), 291 (8, $SnBu_3$), 235 (13, $C_8H_{19}Sn$), 179 (18,

$C_4H_{11}Sn$), 151 (13, SnOMe), and 121 (5, HSn), and the (2*RS*,3*SR*)-ester (0.758 g, 32%), $R_F$ ($Et_2O$) 0.71, $\nu_{max}$ (film) 1735 (C=O) and 1596 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.39 (3H, s, OMe), 3.00 (1H, dq, *J* 11.5 and 7.5 Hz, COCH), 2.70 (1H, d, *J* 11.5 Hz, PhCH), 1.20 (3H, d, *J* 7.5 Hz, Me), and 1.6–0.4 (27H, m, $SnBu_3$), *m/z* 468 (0.05%, $M^+$), 467 (0.05, *M* − H), 437 (0.1, *M* − OMe), 411 (100, *M* − Bu), 395 (2, *M* − $C_4H_9O$), 383 (2, *M* − $C_5H_9O$), 291 (19, $SnBu_3$), 235 (28, $C_8H_{19}Sn$), 179 (54, $C_4H_{11}Sn$), 151 (26, SnOMe), and 121 (27, HSn).

*(2RS,3SR)-2-Methyl-3-phenyl-3-tributyltinpropanoic acid*

The major ester (0.954 g, 2.04 mmol) was added to 6 *M* potassium hydroxide (5 ml) and methanol (35 ml). Ether was added until the mixture formed a single phase. After 10 d water was added, the mixture neutralized with 3 *M* hydrochloric acid, and extracted with dichloromethane. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated in vacuo to give the acid (0.861 g, 93%), $R_F$ ($Et_2O$) 0.70 (streaks), $\nu_{max}$ (film) 3600–2200 (OH), 1709 (C=O) and 1601 and 1496 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 11.86 (1H, br s, $CO_2H$), 7.3–6.8 (5H, m, Ph), 3.08 (1H, dq, *J* 11.5 and 6.5 Hz, COCH), 1.88 (1H, d, *J* 11.5 Hz, PhCH), 1.8–0.3 (30 H, m, remaining H's), *m/z* 397 (40%, *M* − Bu), 291 (34, $SnBu_3$), 235 (40, $C_8H_{19}Sn$), 177 (100, $C_4H_9Sn$), and 121 (44, HSn).

*(3SR,4SR)-3-Methyl-4-phenyl-4-tributyltinbutan-2-one (21)*

This was prepared by the method of Tegner [19]. Methyllithium (2.84 ml of a 0.94 *M* solution in ether) was added to a stirred solution of the acid (0.600 g, 1.32 mmol) in anhydrous ether (5 ml) under nitrogen. After 10 min water (2 ml) was cautiously added and the mixture extracted with ether. The combined extracts were dried ($MgSO_4$) evaporated in vacuo and flash chromatographed eluting with ether/light petroleum (5/95) to give the ketone **21** (0.380 g, 63%).

*(2RS,3SR)-1,3-Diphenyl-2-methyl-3-tributyltinpropane-1-one (47)*

This was prepared by the same method as ketone **21** using the acid (0.490 g, 1.08 mmol) and phenyllithium (2 ml of a 1.10 *M* solution in ether) to give the ketone **47** (0.440 g, 79%), $R_F$ ($Et_2O$) 0.67, $\nu_{max}$ (film) 1685 (C=O) and 1598 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 8.0–7.8 (2H, m, *ortho* Ph H's), 7.5–6.8 (8H, m, other Ph H's), 4.24 (1H, dd, *J* 9 and 6.5 Hz, COCH), 3.22 (1H, d, *J* (Hz, PhCH), and 1.8–0.4 (30H, m, remaining H's), *m/z* 514 (0.05%, $M^+$), 513 (0.1, *M* − H), 457 (100, *M* − Bu), 343 (2, *M* − 3 × Bu), 291 (3, $SnBu_3$), 235 (5, $C_8H_{19}Sn$), 179 (7, $C_4H_{11}Sn$), and 121 (3, HSn).

*(2RS,3RS,4SR)-2,4-Diphenyl-3-methyl-4-tributyltinbutan-2-ol (37)*

This was prepared by the same method as alcohol **13** using ketone **21** (0.100 g, 0.222 mmol) and stirring for 16 h to give the alcohol **37** (0.079 g, 67%), $R_F$ ($Et_2O$) 0.79, $\nu_{max.}$ (film) 3470 (OH) and 1595 and 1492 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (10H, m, 2 × Ph), 2.96 (1H, d, *J* 8.5 Hz, PhCH), 2.8–2.5 (1H, m, Me*CH*), and 1.9–0.3 (34H, m, remaining H's), *m/z* 530 (0.1%, $M^+$), 512 (0.05, *M* − $H_2O$)), 473 (5, *M* − Bu), 455 (5, *M* − (Bu + $H_2O$)), 395 (50, *M* − $C_{10}H_{15}$), 291 (61, $SnBu_3$), 251 (39, $Bu_2SnOH$), 235 (59, $C_8H_{19}Sn$), 207 (71, $C_{16}H_{15}$), and 179 (100, $C_4H_{11}Sn$).

*(2RS,3SR,4RS)-2,4-Diphenyl-3-methyl-4-tributyltinbutan-2-ol (38)*

This was prepared by the same method as alcohol **12** using ketone **47** (0.120 g,

0.234 mmol) to give the alcohol **38** (0.098 g, 79%), $R_F$ ($Et_2O$) 0.69, $\nu_{max.}$ (film) 3460 (br) (OH) and 1595 and 1493 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.4–6.8 (10H, m, 2 × Ph), 2.8–2.4 (2H, m, PhC*H*C*H*), and 1.7–0.3 (34H, m, remaining H's), *m/z* 530 (1%, $M^+$), 512 (0.5, $M - H_2O$), 473 (35, $M$ − Bu), 455 (48, $M - (Bu + H_2O)$), 291 (98, $SnBu_3$), $C_{18}H_{19}Sn$), 207 (100, $C_{16}H_{15}$), and 121 (85, HSn).

*1,3-Dimethyl-1,2-diphenylcyclopropane (**39**) and (**40**)*

These were prepared by the same method as cyclopropane **29** using alcohol **37** (0.220 g, 0.416 mmol) to give the cyclopropanes **39** and **40** (0.084 g, 91%) in a ratio of 1/3. The same cyclopropanes were prepared in 85% yield in a ratio of 1/3 by the same method using alcohol **38** (0.079 g, 0.149 mmol). (1*RS*,2*SR*,3*SR*)-Cyclopropane (**39**), $R_F$ (pentane) 0.17, $\nu_{max}$ ($CCl_4$) 1603 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–7.0 (8H, m, Ph), 6.8–6.6 (2H, m, Ph), 1.84 (1H, d, *J* 2 Hz, PhCH), 1.61 (3H, s, PhC*Me*), 1.52 (3H, d, *J* 5 Hz, Me), and 1.6–1.3 (1H, m, Me*CH*). For 3/1 mixture with cyclopropane **40**: (Found: $M^+$, 222.1392. $C_{17}H_{18}$ calcd. 222.1409), *m/z* 222 (29%, $M^+$), 217 (20, $M$ − Me), 193 (9, $M - C_2H_5$), 178 (11, $M - C_3H_8$), 144 (15, $M - C_6H_6$), 129 (100, $C_{10}H_9$), 117 (20, $C_9H_9$), 115 (24, $C_9H_7$), 91 (48, $C_7H_7$), 78 (24, $C_6H_6$), and 77 (24, Ph). (1*RS*,2*RS*,3*RS*)-Cyclopropane **40**, $R_F$ (pentane) 0.17, $\nu_{max}$ ($CCl_4$) 1603 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–7.0 (10H, m, 2 × Ph), 2.31 (1H, d, *J* 6 Hz, PhCH), 1.6–1.3 (1H, m, Me*CH*), 1.19 (3H, s, PhCMe), and 1.08 (3H, d, *J* 6.5 Hz, Me). For 3/1 mixture with cyclopropane (**39**) (Found: $M^+$, 222.1411. $C_{17}H_{18}$ calcd. 222.1409), *m/z* 222 (8%, $M^+$), 217 (3, $M$ − Me), 193 (9, $M - C_2H_5$), 178 (7, $M - C_3H_8$), 143 (18, $M - C_6H_7$), 129 (60, $C_{10}H_9$), 117 (25, $C_9H_9$), 115 (13, $C_9H_7$), 91 (100, $C_7H_7$), 78 (36, $C_6H_6$), and 77 (48, Ph).

*Methyl 2,3-Diphenyl-2-methyl-3-tributyltinpropanoate (**41** and **42**)*

These were prepared by the same method as ketone **20** using methyl 2,3-diphenyl acrylate (0.714 g, 3.0 mmol) to give the (2*RS*,3*RS*) ester **41** (0.808 g, 50%), $R_F$ ($Et_2O$) 0.78, $\nu_{max.}$ (film) 1729 (C=O) and 1600 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.6–7.0 (10H, m, Ph), 3.50 (3H, s, OMe), 3.54 (1H, s, PhCH), 1.85 (3H, s, Me), and 1.8–0.3 (27H, m, $SnBu_3$), *m/z* 487 (100%, $M$ − Bu), 373 (3, $M - C_{12}H_{27}$), 291 (7, $SnBu_3$), 254 (1, $C_{17}H_{18}O_2$), 235 (11, $C_8H_{19}Sn$), 179 (24, $C_4H_{11}Sn$), and 151 (13, SnOMe), and the (2*RS*,3*SR*)-ester (**42**) (0.416 g, 26%), $R_F$ ($Et_2O$) 0.80, $\nu_{max}$ (film) 1724 (C=O) and 1600 and 1497 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–6.8 (10H, m, 2 × Ph), 3.91 (3H, s, OMe), 3.22 (1H, s, PhCH), 1.54 (3H, s, Me), and 1.7–0.3 (27H, m, $SnBu_3$), *m/z* 487 (94%, $M$ − Bu), 411 (5, $M - C_{10}H_{13}$), 373 (5, $M - C_{12}H_{27}$), 291 (13, $SnBu_3$), 269 (15, $C_{10}H_{13}OSn$), 254 (8, $C_{17}H_{18}O_2$), 235 (20, $C_8H_{19}Sn$), 197 (100, $C_4H_{11}Sn$), and 151 (54, SnOMe).

*(3RS,4RS)-2,3-Dimethyl-3,4-diphenyl-4-tributyltinbutan-2-ol (**43**)*

Methyllithium (0.16 ml of a 1.55 *M* solution in ether) was added to a stirred solution of the ester **41** (0.064 g, 0.118 mmol) in anhydrous ether (5 ml) under nitrogen at −23°C. After 1 h saturated ammonium chloride solution was added and the mixture extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and purified by preparative thin-layer chromatography eluting with ether/light petroleum (5/95) to give the alcohol **43** (0.030 g, 47%), $R_F$ ($Et_2O$) 0.77, $\nu_{max}$ (film) 3590 and 3460 (br) (OH) and 1598 and 1492 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.8–7.5 (2H, m, Ph), 7.5–7.0 (8H, m, Ph), 2.86 (1H, s, PhCH), 1.69 (3H, s, Me),

1.4–0.1 (34H, s, remaining H's), *m/z* 544 (1%, $M^+$), 526 (1, $M - H_2O$), 487 (7, $M - Bu$), 471 (4, $M - (Bu + H_2O)$), 373 (1, $M - C_{12}H_{27}$), 353 (1, $M - C_{14}H_{23}$), 315 (2, $M - C_{18}H_{33}$), 291 (43, $SnBu_3$), 251 (30, $Bu_2SnOH$), 236 (100, $C_{18}H_{20}$), 235 (35, $C_8H_{19}Sn$), 221 (42, $C_{17}H_{17}$), 179 (50, $C_4H_{11}Sn$), 137 (11, $CH_5Sn$), and 121 (15, HSn).

*(3RS,4SR)-2,3-Dimethyl-3,4-diphenyl-4-tributyltinbutan-2-ol (**44**)*

Methyllithium (0.32 ml of a 1.55 *M* solution in ether) was added to a stirred solution of the ester **42** (0.130 g, 0.239 mmol) in anhydrous ether (5 ml) under nitrogen. After 5 h water was cautiously added and the mixture extracted with ether. The combined extracts were dried ($MgSO_4$), evaporated in vacuo and returned to the same reaction conditions for 5 h. The same work-up followed by flash chromatography eluting with ether/light petroleum (5/95) gave the alcohol **44** (0.032 g, 25%), $R_F$ ($Et_2O$) 0.73, $\nu_{max.}$ (film) 3620 and 3450 (br) (OH) and 1598 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–6.7 (10H, m, 2 × Ph), 3.79 (1H, s, PhCH), 1.67 (3H, s, Me), 1.34 (3H, s, Me), 1.01 (3H, s, Me), and 1.9–0.3 (28H, m, remaining H's), *m/z* 544 (0.5%, $M^+$), 526 (1, $M - H_2O$), 487 (16, $M - Bu$), 471 (4, $M - (Bu + H_2O)$), 373 (1, $M - C_{12}H_{27}$), 353 (1, $M - C_{14}H_{23}$), 315 (3, $M - C_{18}H_{33}$), 291 (46, $SnBu_3$), 251 (100, $Bu_2SnOH$), 236 (86, $C_{18}H_{20}$), 235 (43, $C_8H_{19}Sn$), 221 (79, m $C_{17}H_{17}$), 179 (57, $C_4H_{11}Sn$), 137 (26, $CH_5Sn$), and 121 (19, HSn).

*trans-1,3-Diphenyl-1,2,2-trimethylcyclopropane (**45**)*

This was prepared by the same method as cyclopropane **29** using alcohol **43** (0.103 g, 0.189 mmol) to give the cyclopropane **45** (0.043 g, 96%), $R_F$ (pentane) 0.18, $\nu_{max}$ ($CCl_4$) 1599 and 1496 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.4–7.2 (10H, m, 2 × Ph), 2.30 (1H, s, PhCH), 1.22 (3H, s, Me), 1.17 (3H, s, Me), and 0.97 (3H, s, Me) (Found: $M^+$, 236.1556. $C_{18}H_{20}$ calcd. 236.1564), *m/z* 236 (100%, $M^+$), 221 (73, $M - Me$), 143 (74, $M - C_7H_9$), 131 (24, $M - C_8H_9$), 115 (19, $C_9H_7$), 105 (31, $C_8H_9$), 91 (68, $C_7H_7$), and 77 (16, Ph).

*cis-1,3-Diphenyl-1,2,2-trimethylcyclopropane (**46**)*

This was prepared by the same method as cyclopropane **29** using alcohol **44** (0.063 g, 0.116 mmol) to give the cyclopropane **46** (0.020 g, 73%), $R_F$ (pentane) 0.18, $\nu_{max}$ ($CCl_4$) 1601 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CDCl_3$) 7.4–7.1 (8H, m, Ph), 6.85–6.8 (2H, m, Ph), 1.93 (1H, s, PhCH), 1.53 (3H, s, Me), 1.46 (3H, s, Me), and 1.10 (3H, s, Me *cis* to Ph) (Found: $M^+$, 236.1578. $C_{18}H_{20}$ calcd. 236.1565), *m/z* 236 (100%, $M^+$), 221 (85, $M - Me$), 1243 (81, $M - C_7H_9$), 131 (20, $M - C_8H_9$), 128 (19, $M - C_8H_{12}$), 115 (20, $C_9H_7$), 104 (23, $C_8H_9$), 91 (64, $C_7H_7$), and 77 (18, Ph).

*1,3-Diphenyl-2-methyl-3-tributyltinpropan-1-ol (**48** and **49**)*

Sodium borohydride (0.1 g) in ethanol (10 ml) was added to a stirred solution of the ketone **47** (0.132 g, 0.257 mmol) in ethanol (10 ml). After 48 h water was added and the mixture extracted with ether. The combined extracts were washed with 3*N* hydrochloric acid, saturated sodium hydrogencarbonate solution, brine and water, dried ($MgSO_4$), evaporated in vacuo, and flash chromatographed eluting with ether/light petroleum (10/90) to give; (1*RS*,2*SR*,3*RS*)-alcohol **48** (0.105 g, 79%), $R_F$ ($Et_2O$) 0.77, $\nu_{max}$ (film) 3430 (br) (OH) and 1601, 1593 and 1492 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.4–6.9 (10H, m, 2 × Ph), 4.61 (1H, br d, *J* 4.5 Hz, C*H*OH), 2.8–2.4 (1H, m,

PhCCH), 2.30 (1H, br s, OH), and 1.7–0.3 (30H, m, remaining H's), *m/z* 516 (1%, $M^+$), 459 (15, $M - Bu$), 441 ($M - (Bu + H_2O)$), 345 (1, $M - C_{12}H_{27}$), 291 (31, $SnBu_3$), 251 (41, $Bu_2SnOH$), 235 (38, $C_8H_{19}Sn$), 208 (100, $C_{16}H_{16}$), 193 (48, $C_{15}H_{13}$), 179 (75, $C_4H_{11}Sn$), 137 (17, HOSn), and 121 (34, HSn), and (1*RS*,2*RS*,3*SR*)-alcohol (**49**) (0.025 g, 19%), $R_F$ ($Et_2O$) 0.78, $\nu_{max.}$ (film) 3440 (br) (OH) and 1597 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.4–7.0 (10H, m, 2 × Ph), 4.62 (1H, br s, C*H*OH), 2.83 (1H, d, *J* 12 Hz, PhCH), 2.5–2.2 (1H, m, PhCCH), and 1.7–0.3 (31H, m, remaining H's), *m/z* 516 (0.5%, $M^+$), 459 (47, $M - Bu$), 441 (1, $M - (Bu + H_2O)$), 345 (2, $M - C_{12}H_{27}$), 291 (18, $SnBu_3$), 251 (42, $Bu_2SnOH$), 235 (20, $C_8H_{19}Sn$), 208 (100, $C_{16}H_{16}$), 193 (20, $C_{15}H_{13}$), 179 (37, $C_4H_{11}Sn$), 137 (12, HOSn), and 121 (18, HSn).

*(1RS,2RS)-1,2-Diphenyl-3-methylcyclopropane (50)*

This was prepared by the same method as cyclopropane **29** using alcohol **48** (0.120 g, 0.233 mmol) to give the cyclopropane **53** (0.047 g, 97%), $R_F$ (pentane) 0.20, $\nu_{max.}$ ($CCl_4$) 1600 and 1490 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.5–7.0 (10H, m, 2 × Ph), 2.46 (1H, dd, *J* 10 and 6 Hz, PhC*H*, Ph *cis* to Me), 2.10 (1H, t, *J* 6 Hz, PhC*H*, Ph *trans* to Me), 1.7–1.3 (1H, m, MeC*H*), and 1.04 (3H, d, *J* 6.5 Hz, Me) (Found: $M^+$, 208.1255. $C_{16}H_{16}$ calcd. 207.1252), *m/z* 208 (27%, $M^+$), 193 (23, $M - Me$), 179 (10, $M - C_2H_5$), 178 (12, $M - C_2H_6$), 130 (28, $M - C_6H_6$), 115 (100, $C_9H_7$), and 91 (60, $C_7H_7$).

*(1RS,2SR)-1,2-Diphenyl-3-exo-methylcyclopropane (51)*

This was prepared by the same method as cyclopropane **29** using alcohol **49** (0.046 g, 0.089 mmol) to give the cyclopropane **51** (0.016 g, 86%), $R_F$ (pentane) 0.20, $\nu_{max.}$ ($CCl_4$) 1602 and 1494 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.7 (10H, m, 2 × Ph), 2.15 (2H, d, *J* 5 Hz, PhCH), 1.67 (1H, m, MeC*H*), and 1.42 (3H, d, *J* 6 Hz, Me) (Found: 208.1251. $C_{16}H_{16}$ calcd. 208.1252), *m/z* 208 (30%, $M^+$), 193 (28, $M - Me$), 179 (27, $M - Me$), 179 (27, $M - C_2H_5$), 178 ($M - C_2H_6$), 130 (20, $M - C_6H_6$), 115 (76, $C_9H_7$), and 91 (100, $C_7H_7$).

*3-Methyl-4-phenyl-4-tributyltinbutan-2-ol (52 and 53)*

These were prepared by the same method as alcohol **48** using ketone **20** (0.451 g, 1.0 mmol) and stirring for 5 h to give the (1*RS*,2*SR*,3*SR*)-alcohol (**52**) (0.302 g, 67%), $R_F$ ($Et_2O$) 0.73, $\nu_{max}$ (film) 3400 (br) (OH) and 1599 and 1495 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 3.8–3.4 (1H, m, C*H*OH), 2.6–2.0 (2H, m, PhC*HCH*), 1.67 (1H, s, OH), and 1.8–0.3 (33H, m, remaining H's), *m/z* 454 (0.5%, $M^+$), 397 (100, $M - Bu$), 291 (24, $SnBu_3$), 251 (31, $Bu_2SnOH$), 235 (28, $C_8H_{19}Sn$), and 179 (44, $C_4H_{11}Sn$), and the (1*RS*,2*RS*,3*RS*)-alcohol (**53**) (0.125 g, 28%), $R_F$ ($Et_2O$) 0.73, $\nu_{max.}$ (film) 3480 (br) (OH) and 1600 and 1497 $cm^{-1}$ (Ph), $\delta$ ($CCl_4$) 7.3–6.8 (5H, m, Ph), 4.0–3.7 (1H, m, C*H*OH), 2.61 (1H, d, *J* 11.5 Hz, PhCH), 2.3–1.9 (1H, m, PhCCH), and 1.8–0.3 (34H, m, remaining H's), *m/z* 397 (92%, $M - Bu$), 291 (45, $SnBu_3$), 251 (38, $Bu_2SnOH$), 235 (50, $C_8H_{19}Sn$), and 179 (100, $C_4H_{11}Sn$).

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