# Selective Electrophilic Additions of Mixed Bifunctionalized Trimethylenemethane Dianion Synthons

George Majetich,* Hisaya Nishidie and Yong Zhang
Department of Chemistry, The University of Georgia, Athens, Georgia, USA, 30602

Three trimethylenemethane dianion synthons showed a profound divergence of reactivity, based upon the choice of catalyst employed.

In 1979 Bates and co-workers showed that the dianion of isobutene 1 reacts with electrophiles to give functionalized open-chain compounds by first functionalizing one allylic anion and then adding an additional electrophile to the remaining anion (cf. 1 —→ 2, Scheme 1).[1] When two electrophilic species
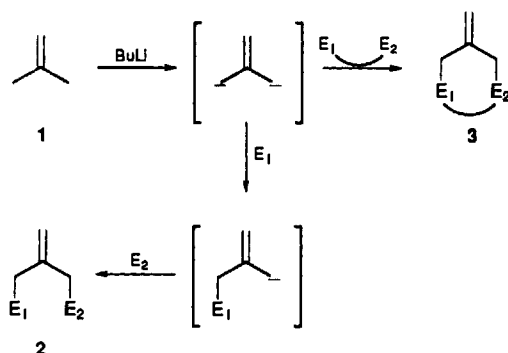
Scheme 1

are linked together, this dianion/dielectrophile strategy results in the formation of carbocyclic rings (cf. 1 —→ 3). Unfortunately, reaction of the dianion 1 cannot be controlled to allow it to react successively with two different electrophiles, thus limiting this methodology.

Allylstannanes[2] and allylsilanes[3] react with a wide variety of electrophiles, and these functionalities have been widely used as latent allylic nucleophiles for both inter- and intra-molecular carbon–carbon bond formation. Not surprisingly, these reactive functionalities have proven useful for numerous dianionic synthons of isobutene. For example, in 1983 Wuest and co-workers[4] found that 2-methylidenepropane-1,3-diylbis-(triphenylstannane) 4 is slowly converted into 1,1,1,5,5,5-hexachloro-3-methylidenepentane 5 in 65% yield via a radical process [eqn. (1)].† Since then others have used related reagents for carbocyclic formation. Trost pioneered the use of trimethylenemethane equivalents, such as 6, for the one-step preparation of cyclopentane rings via 1,3-dipolar additions with electrophilic olefins [eqn. (2)].[6] Degl'Innocenti and co-workers showed that the allylbisstannane 7 reacts with diacyl dichlorides to produce cyclic diones, independent of ring size {cf. 8 [eqn. (3)] and 12 [eqn. (7)]}.[7] Other workers have developed similar two-step sequences differing only in the manner in which the various nucleophilic and/or electrophilic species are generated in situ.‡[8]

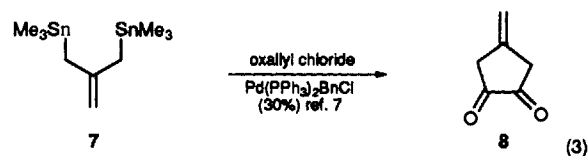† Recently Keck and Ueno have found that bis-allylstannane reagents such as 4 react with standard electrophiles.[5]
‡ 2-Trimethylsilylmethyl-π-allylnickel halides readily couple with alkyl halides to produce functionalized allylsilanes.[9]
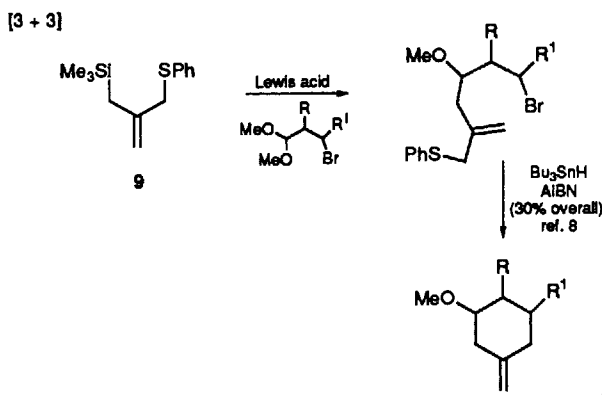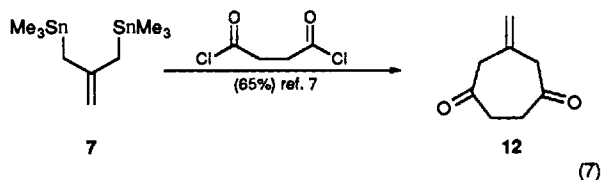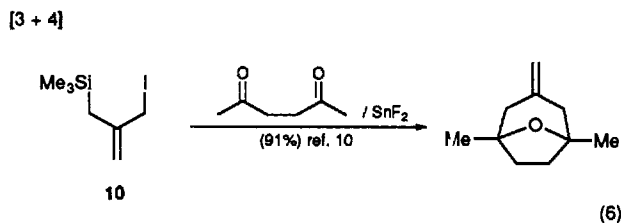
(1)

[3 + 2]

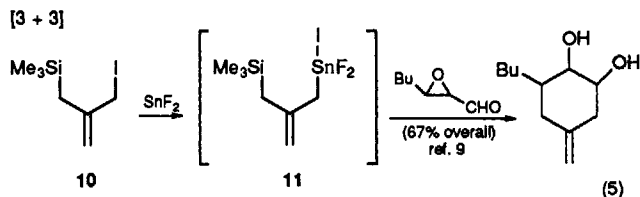(2)

(3)

[3 + 3]
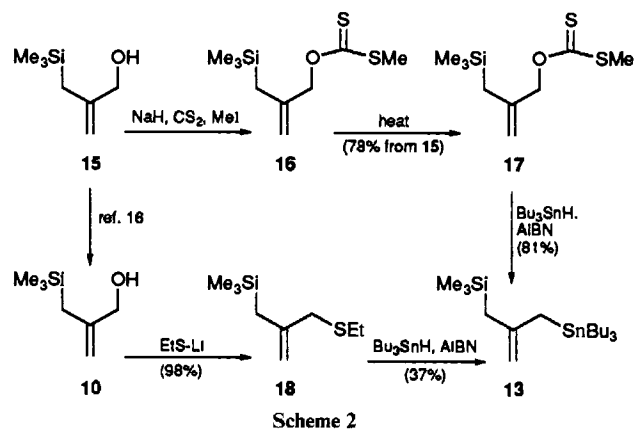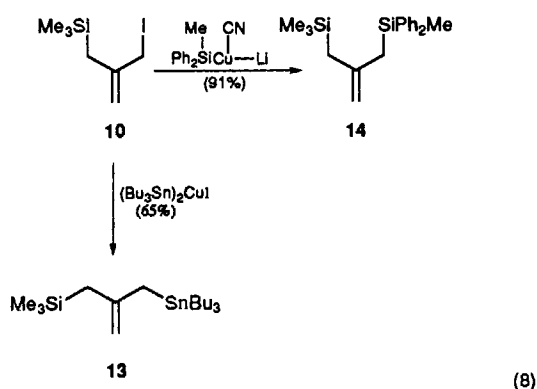
(4)

[3 + 3]

(5)

[3 + 4]

(6)

(7)
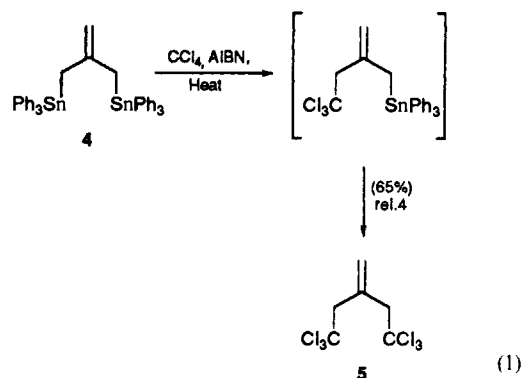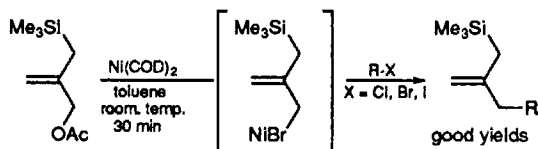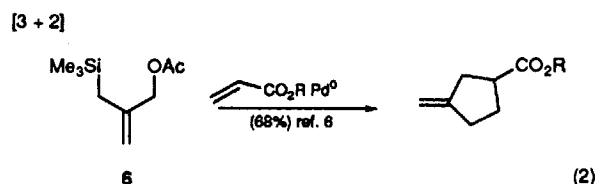
Molander and Shubert have exploited mixed allylstannane/allylsilane isobutene-based reagents for carbocyclic formation [eqns. (5) and (6)]. In their studies, the allylic iodide **10** was treated with SnF₂ to generate a reactive allylstannane intermediate (*cf.* **11**) *in situ*, which then could be used for the preparation of five-, six-, seven- and/or eight-membered rings.[10]

During our study directed towards a synthesis of the linearly fused triquinane hirsutene we found that a trimethylallylsilane moiety reacts more rapidly under Lewis acid catalysis than the analogous methyldiphenylallylsilane.[11] This observation prompted us to prepare the mixed bifunctionalized reagents **13** and **14** on the premise that the differences in the reactivity of the functionalities present would allow us to control the order with which they react.§

Results and Discussion ¶

Reagents **13** and **14** were prepared from 2-trimethylsilylmethyl-prop-2-en-1-ol (**15**)[13] as shown in eqn. (8) and Scheme 2, respectively. Reaction of the cuprate reagent derived from chloromethyldiphenylsilane[14] and iodide **10**[15] gave a 91% yield of 3-methyldiphenylsilyl-2-[(trimethylsilyl)methyl]propane **14**. The preparation of 3-tributylstannyl-2-[(trimethylsilyl)meth-

(8)

---

§ For rate constant comparing the reactivity of allylsilanes, silyl enol ethers and allylstannnes, see ref. 12.

¶ All yields are isolated yields. No attempt was made to optimize the transformations reported.

Scheme 2

yl]propene **13** was less direct.‖ Although reaction of the requisite cuprate reagent and the iodide **10** generated **13**, its purification either chromatographically or by distillation was problematic. Fortunately, the reagent **13** could be prepared cleanly from either the dithiocarbamate **17** or the sulfide **18** (Scheme 2). Treatment of the alcohol **15** with sodium hydride and carbon disulfide, followed by the addition of iodomethane, produced the xanthate **16** which was thermally rearranged to **17**. Conversion of this dithiocarbamate, or allylic sulfide **18**, into the reagent **13** was achieved using a free radical process. Although less direct than the cuprate coupling, these alternative sequences allowed **13** to be prepared free of contaminants.

We were confident that the differences in the reactivity of allylstannanes and allylsilanes would permit their differentiation in our bifunctional reagent. This conjecture proved to be valid. For example, treatment of mixed allylsilane/allylstannane **13** with fluoride ion resulted in the selective reaction of the allylsilane moiety (*cf.* **19**), since allylstannanes are inert under these conditions. In contrast, we observed that heating **13** at temperatures > 150 °C causes only the allylstannane moiety to react (*cf.* **20**).** This was not surprizing since allylstannanes are known to react at elevated temperatures,[16] whereas allysilanes are thermally stable.††

(9)
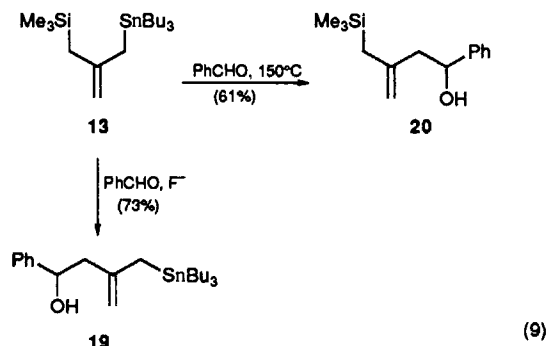
Allylsilanes and allylstannanes both react with electrophiles on exposure to Lewis acid catalysts. We speculated that the more reactive nucleophilic functionality (the allylstannane) would react preferentially using a mild Lewis acid. Indeed,

---

‖ At first we made 3-trimethylsilyl-2-[(trimethylstannyl)methyl]propene by coupling the iodide **10** with (Me₃Sn)₂CuI. In our hands, however, this product was difficult to purify, encouraging us to substitute the highly reactive trimethylstannyl moiety with a more stable tributylstannyl one.

** Extensive work showed that if reagent **13** was contaminated with organotin-by-products this condensation was not observed.

†† Organostannanes also react under high pressure, see ref. 17. Our results suggest that reagent **13** should also exploit these experimental conditions.

reaction of allylstannane/allylsilane **13** with benzaldehyde in the presence of triethylaluminium, a weak Lewis acid, results in the selective reaction of the stannane moiety [**13** ⟶ **20**, eqn. (10)].

(10)
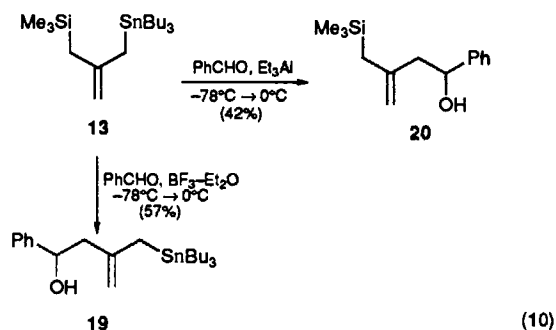
Stronger Lewis acids, such as titanium tetrachloride, stannous tetrachloride, iron trichloride, magnesium bromide, zinc chloride or trimethylsilyl triflate were also studied but gave unsatisfactory results. Inexplicably, the reaction of reagent **13** at low temperatures with a stoichiometric amount of boron trifluoride–diethyl ether resulted in the exclusive reaction of the allylsilane moiety (**14** ⟶ **19**).

The substrate **14** contains two allylsilane moieties, both of which will react with equal likelihood using fluoride ion catalysis but which we expected would demonstrate a Lewis acid dependency. This proved to be the case as treatment of **14** with trimethylaluminium resulted in the reaction of only the trimethylallylsilane unit [cf. **21**, eqn. (11)] leaving the less reactive methyldiphenylallylsilane unit for further use (i.e., **21** ⟶ **22**).

(11)
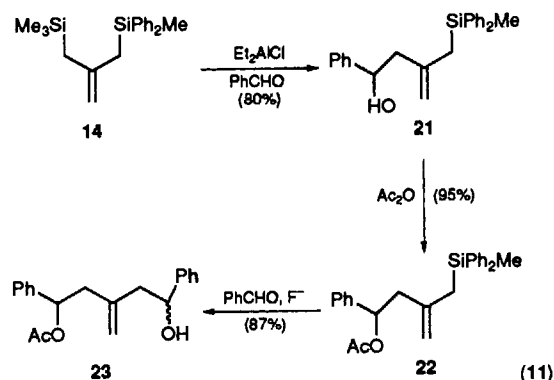
The selectivity demonstrated by these bifunctional reagents has considerable synthetic potential. For example, the use of these reagents for the formation of polycyclic systems by means of a tandem inter-/intra-molecular strategy, as generalized in eqn. (12), is the focus of on-going work.

Experimental

General.—All reactions were run under an inert atmosphere of nitrogen and monitored by TLC analysis until the starting material was completely consumed. Unless otherwise indicated, all ethereal work-ups consisted of the following procedure: the reaction was quenched at room temperature with saturated aqueous ammonium chloride. The organic solvent was removed under reduced pressure on a rotary evaporator and the residue was taken up in diethyl ether, washed with brine and dried over anhydrous magnesium sulfate. Filtration, followed by concentration at reduced pressure on a rotary evaporator and at 1 Torr to constant weight, afforded a crude residue which was purified

(12)

M = Sn or Si
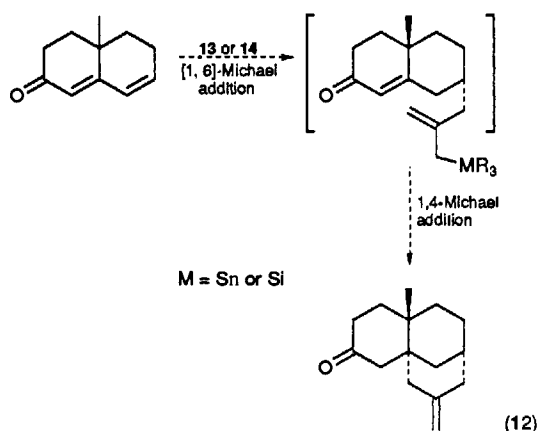
by flash chromatography using NM silica gel 60 (230–400 mesh ASTM) and distilled reagent grade solvents. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker 250 spectrometer at 250 MHz and at 62.7 MHz, respectively. Chemical shifts are reported relative of CDCl$_3$ as an internal standard; *J* values are recorded in Hz. Microanalysis was performed by Atlantic Microlab, Inc., Atlanta, GA.

3-Tributylstannyl-2-[(trimethylsilyl)methyl]propene **13**.—(a) via *Cuprate coupling.* To tributyltin hydride (786 mm^3,‡‡ 2.83 mmol) in dry tetrahydrofuran (THF; 8 cm^3) at 0 °C was added dropwise butyllithium (2.5 mol dm^{-3} in hexanes; 1.13 cm^3, 2.83 mmol). The resulting mixture was stirred at 0 °C for 2 h, after which it was transferred (*via* a cannula) to a suspension of copper(I) cyanide (270 mg, 1.42 mmol) in dry THF (2 cm^3) at 0 °C. After 30 min, the reaction mixture was diluted with dry THF (5 cm^3), cooled to − 10 °C, and treated with the iodide **10** in dry THF (3 cm^3). The resulting mixture was stirred at − 10 °C for 90 min after which it was quenched by being poured onto saturated aqueous ammonium chloride and saturated aqueous sodium carbonate (1:1; 8 cm^3); it was then extracted with ether (3 × 25 cm^3). The combined extracts were dried (MgSO$_4$), filtered and concentrated. Purification of the residue by chromatography on silica gel (elution with hexanes) gave **13** (319 mg, 65%) which was homogenous by TLC analysis (hexanes, R_F **10** 0.68, R_F **13** 0.87) (Found: C, 54.8; H, 10.3. C$_{19}$H$_{42}$SiSn requires C, 54.68; H, 10.14%); δ_H[250 MHz; CDCl$_3$] 0.04 [9 H, s, (CH$_3$)$_3$Si], 0.91 [9 H, t, *J* 7, (CH$_2$-CH$_2$CH$_2$C*H*$_3$)$_3$], 1.20–1.78 [20 H, m, (C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$)$_3$ and (CH$_3$)$_3$SiC*H*$_2$], 2.28 [2 H, s, (CH$_3$)$_3$SnC*H*$_2$], 4.62 (1 H, s, *H*C=) and 4.72 (1 H, s, HC=).

(b) via *The dithiocarbamate route.* The alcohol **15** (1.00 g, 6.93 mmol) was treated with sodium hydride (80%; 229 mg, 7.62 mmol) dissolved in dry THF (15 cm^3). Carbon sulfide (500 mm^3, 8.32 mmol) was added to the mixture which was then stirred at 0 °C for 60 min. After this the mixture was treated with iodomethane (650 mm^3, 10.40 mmol) and stirred for an additional 60 min at 0 °C. Standard ethereal work-up gave the crude xanthate (1.21 g; TLC analysis: hexane–ether, 10:1, R_F **15** 0.21, R_F **16** 0.83) that was used without purification or characterization.

The crude xanthate was dissolved in dry benzene (20 cm^3) and the solution refluxed for 7 h. The reaction mixture was then cooled to room temperature, concentrated and chromatographed (elution with hexane–ether, 50:1) to provide the dithiocarbamate **17** (1.27 g, 78%) which was homogeneous by TLC analysis [hexane–ether, 50:1, R_F **16** 0.57, R_F **17** 0.40].

---

‡‡ 1 mm^3 = 1 μl.

The dithiocarbamate 17 (1.22 g, 5.18 mmol) was dissolved in toluene (20 cm³) and the solution heated to reflux. To the reaction mixture was added tributyltin hydride (1.41 dm³, 5.08 mmol) and azoisobutyronitrile (AIBN) (84 mg, 0.51 mmol) over a 30 min period. After the resulting mixture had been refluxed for 24 h it was evaporated under reduced pressure and the residue (2.59 g) was chromatographed on silica gel (elution hexanes, R_F 17 0.18, R_F 13 0.31) to give the reagent 13 (1.75 g, 81%) which was identical with that prepared previously.

(c) via *The sulfide route.* Ethanethiol (520 mm³, 7.01 mmol) was slowly added to butyllithium (2.5 mol dm⁻³; 3.0 cm³, 7.36 mmol) in THF (20 cm³) at 0 °C and the mixture then stirred for 30 min. The allylic iodide 10 was dissolved in dry THF (3 cm³) the solution added to the mixture over a 5-min period. The resulting mixture was stirred at 0 °C for 1 h and then warmed to room temperature over a 40-min period. Standard ethereal work-up, followed by chromatography (elution with hexanes), gave the sulfide 18 (1.03 g, 98%) which was homogeneous by TLC analysis (hexanes, R_F 10 0.74, R_F 18 0.56); δ_H[250 MHz; CDCl₃], 0.03 [9 H, s, (CH₃)₃Si], 1.10 [3 H, t, J 7, CH₂(CH₃)], 1.70 [2 H, s, (CH₃)₃SiCH₂], 2.22 (2 H, q, J 7, SCH₂CH₃), 3.10 (2 H, s, CHCH₂S), 4.19 (1 H, s, HC=) and 4.36 (1 H, s, HC=).

The sulfide 18 (1.03 g, 5.47 mmol) was dissolved in toluene (30 cm³) and the resulting solution was heated to reflux. To the reaction mixture was added tributyltin hydride (1.49 cm³, 5.36 mmol) and AIBN (90 mg, 0.54 mmol) over a 30-min period. The resulting mixture was refluxed for 12 h after which it was evaporated under reduced pressure and the residue was chromatographed on silica gel (elution with hexanes) to give the reagent 13 (843 mg, 37%), identical with that previously described.

3-Methyldiphenylsilyl-2-[(trimethylsilyl)methyl]propene 14. —Phenyldimethylchlorosilane (3.50 g, 15.00 mmol) was added to finely cut lithium metal (250 mg, 36.00 mmol) suspended in dry THF (20 cm³). After being stirred for 90 min at −10 °C, the solution turned dark red. Continued vigorous stirring for 3 h produced a brownish solution which was transferred (*via* a cannula) to a suspension of copper(I) cyanide (600 mg, 6.70 mmol) in dry THF (5 cm³) at 0 °C. After 30 min at −78 °C, the reaction mixture was allowed to warm to −10 °C. The iodide 10 (1.54 g, 6.70 mmol) in dry THF (5 cm³) was added to it and the resulting mixture was stirred at −10 °C for 60 min. After this it was quenched by being poured onto a mixture of saturated aqueous ammonium chloride and saturated aqueous sodium carbonate (1:1; 30 cm³) and extracted with ether (4 × 30 cm³ portions). The combined extracts were dried (MgSO₄), filtered and concentrated. Purification of the residue by chromatography on silica gel (elution with hexanes) gave 14 (1.79 g, 91%) which was homogeneous by TLC analysis (hexanes, R_F 10 0.77, R_F 14 0.61) (Found: C, 73.8; H, 8.7. C₂₀H₂₈Si₂ requires C, 74.00; H, 8.69%); δ_H(250 MHz; CDCl₃) 0.03 [9 H, s, (CH₃)₃Si], 0.66 [3 H, s, CH₃Si(C₆H₅)₂], 1.36 [2 H, s, (CH₃)₃SiCH₂], 2.09 [2 H, s, CH₄(C₆H₅)₂SiCH₂], 4.45 (2 H, s, H₂C=) and 7.35–7.65 [10 H, m, (C₆H₅)₂].

Fluoride Ion-promoted Condensation of 13 *with Benzaldehyde.*—To tetrabutylammonium fluoride trihydrate (313 mg, 1.20 mmol) which had been stored *in vacuo* for 30 min was added dry DMF (2 cm³) and a few activated 4 Å molecular sieves. After 15 min, the solution was transferred to a reaction vessel containing 4 Å molecular sieves (100 mg) and benzaldehyde (55 mg, 0.90 mmol). The reagent 13 (417 mg, 1.00 mmol) in dry DMF (10 cm³) was added dropwise over 1 h using a syringe pump to the mixture which was then stirred at room temperature for 2 h and finally quenched with water. Standard ethereal work-up provided a crude residue that was purified by chromatography on silica gel (elution with hexanes–ether, 2:1)

to afford the alcohol 19 (32.8 g, 73%) which was homogeneous by TLC analysis (hexanes–ether, 1:1, R_F PhCHO 0.79, R_F 19 0.32); ν_{max}(film)/cm⁻¹ 3350–3200 (OH); δ_H(250 MHz; CDCl₃) 0.92 [9 H, t, J 7, (CH₂CH₂CH₂CH₃)₃], 1.20–1.78 [18 H, m, (CH₂CH₂CH₂CH₃)₂], 2.40–2.60 (1 H, m, CHCH₂–C=), 2.42 (2 H, s, CH₂SnR₃), 3.72 (1 H, br s, OH), 4.81–4.90 (1 H, m, C₆H₅CHOH), 5.00 (1 H, s, CH=), 5.20 (1 H, s, CH=) and 7.30–7.50 (5 H, m, C₆H₅).

Heat-promoted Condensation of 13 *with Benzaldehyde.* —To a solution of benzaldehyde (37 mg; 0.34 mmol) in dry *p*-xylene (3 cm³) was added the reagent 13 (100 mg, 0.34 mmol). After being refluxed for 24 h (150 °C), the reaction mixture was cooled to 0 °C, diluted with ether (25 cm³) and washed with saturated aqueous ammonium chloride. Standard ethereal work-up gave a crude residue which was purified by chromatography on silica gel (elution with hexanes–ether, 2:1) to give the adduct 20 (49 mg, 61%) which was homogeneous by TLC analysis (hexanes–ether, 1:1, R_F PhCHO 0.79, R_F 20 0.35); ν_{max}(film)/cm⁻¹ 3400–3150 (OH); δ_H(250 MHz; CDCl₃) 0.07 [9 H, s, (CH₃)₃Si], 1.53–1.65 [2 H, m, CH₂Si(CH₃)₃], 2.25–2.50 (3 H, m, CH₂C= and OH), 4.70–4.90 (3 H, m, CH₂= and CHOH) and 7.20–7.50 (5 H, m, C₆H₅).

Triethylaluminium-catalysed Condensation of 13 *with Benzaldehyde.*—To a solution of benzaldehyde (159 mg, 1.50 mmol) dry methylene dichloride (7 cm³) was added Et₃Al (1.9 mol dm⁻³, 2.50 mmol) at −78 °C. After being stirred for 4 h at −78 °C, the reaction mixture was warmed to 0 °C and stirred at this temperature for 90 min. After this it was quenched with saturated aqueous ammonium chloride (2 cm³) and treated to a standard ethereal work-up to give a crude residue. This was purified by chromatography on silica gel (elution with hexanes–ether, 3:1) to give the adduct 20 (24 mg, 42%), identical with that prepared previously.

BF₃·Et₂O-Catalysed Condensation of 13 *with Benzaldehyde.*—To a solution of benzaldehyde (171 mg, 1.61 mmol) in dry methylene dichloride (7 cm³) was added BF₃·Et₂O (330 mm³, 2.8 mmol) at −78 °C. After being stirred for 3 h at −78 °C, the reaction mixture was quenched with saturated aqueous sodium hydrogen carbonate (2 cm³) and subjected to a standard ethereal work-up to give a crude residue. This was purified by chromatography on silica gel (elution with hexanes–ether, 3:1) to give the adduct 19 (35 mg, 57%) which was identical with that prepared previously.

Et₂AlCl-Catalysed Condensation of 14 *and Benzaldehyde.*—To a solution of benzaldehyde (444 mg, 4.18 mmol) and 14 (1.13 g, 3.48 mmol) in dry methylene dichloride (20 cm³) at −78 °C was added Et₂AlCl (1.93 cm³, 3.48 mmol). After being stirred for 1 h at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride (5 cm³) and subjected to a standard ethereal work-up to give a crude residue. This was purified by chromatography on silica gel (elution with hexanes–ether, 3:1) to give the alcohol 21 (522 mg, 42%) which was homogeneous by TLC analysis (hexanes–ether, 3:1, R_F PhCHO 0.56; R_F 21 0.36); δ_H(250 MHz; CDCl₃) 0.72 [3 H, s, CH₃Si(C₆H₅)₂], 2.20–2.50 (4 H, m, CH₂CCH₂), 4.77 (2 H, br s, CH₂=), 7.20–7.70 [15 H, m, (C₆H₅)₂ and C₆H₅CH].

Acetylation of 21.—To the alcohol 21 (522 mg, 1.46 mmol) dissolved in pyridine (2 cm³) was added acetic anhydride (1 cm³). The resulting mixture was stirred for 13 h at room temperature and then diluted with ether (50 cm³). The organic phase was washed with saturated aqueous copper(II) sulfate (3 × 50 cm³) and brine (15 cm³), dried (MgSO₄), filtered and concentrated. The crude residue was chromatographed on silica gel (elution with hexanes–ether, 3:1) to furnish the acetate 22

(558 mg, 95%), which was homogeneous by TLC analysis (hexanes–ether, 3:1, R_F **21** 0.36; R_F **22** 0.69); δ_H[250 MHz; CDCl$_3$] 0.72 [3 H, s, CH_3Si(C$_6$H$_5$)$_2$], 2.12 (3 H, s, CH_3CO), 2.20–2.55 (4 H, m, CH$_2$CCH$_2$), 4.77 (2 H, br s, CH$_2$=), 5.92–6.05 (1 H, m, CHOAc) and 7.20–7.75 [15 H, m, (C$_6$H$_5$)$_2$ and C$_6$H$_5$CH].

Fluoride Ion-promoted Condensation of **21** *and Benzaldehyde.*—To tetrabutylammonium fluoride trihydrate (4.35 mg, 1.67 mmol) which had been stored *in vacuo* for 30 min was added dry DMF (3 cm^3) and a few activated 4 Å molecular sieves. After 15 min, the solution was transferred to a reaction vessel containing 4 Å molecular sieves (100 mg) and benzaldehyde (133 mg, 1.25 mmol). A solution of acetate **22** (558 mg, 1.39 mmol) in dry DMF (10 cm^3) was added dropwise to this solution over 1 h using a syringe pump. The resulting mixture was stirred at room temperature for 3 h and then quenched with water. Standard ethereal work-up provided a crude residue that was purified by chromatography on silica gel (elution with hexanes–ether, 3:1) to afford the alcohol **23** (375 mg, 87%) which was homogeneous by TLC analysis [hexanes–ether (3:1), R_F PhCHO 0.69; R_F **23** 0.22); δ_H(250 MHz; CDCl$_3$) 2.13 (3 H, s, CH$_3$CO), 2.30–2.55 (4 H, m, CH$_2$CCH$_2$), 3.86 (1 H, br s, OH), 4.80 (2 H, s, CH$_2$=), 5.10–5.20 (1 H, m, CHOH), 5.95–6.02 (1 H, m, CHOAc) and 7.15–7.50 [10 H, m, (C$_6$H$_5$)$_2$ and C$_6$H$_5$CH].

References

1 R. B. Bates, W. A. Beavers, B. Gordon, III and N. S. Mills, *J. Org. Chem.*, 1979, **44**, 3800.

2 For leading examples of allylstannane chemistry see: (*a*) Y. Yamamoto, *Acc. Chem. Res.*, 1987, **20**, 243; (*b*) G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, 1982, **104**, 5829.

3 I. Fleming, J. Dunogues and R. Smithers, *Org. React.*, 1989, **37**, 57.

4 S. Chandrasekhar, S. Latour, J. D. Wuest and B. Zacharie, *J. Org. Chem.*, 1983, **48**, 3810.

5 (*a*) G. E. Keck and A. Palani, *Tetrahedron Lett.*, 1993, **34**, 3223; (*b*) H. Sano, M. Okara and Y. Ueno, *Synthesis*, 1984, **11**, 933.

6 For a review, see: B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1.

7 A. Degl'Innocenti, P. Dembech, A. Mordini, A. Ricci and G. Seconi, *Synthesis*, 1991, 267.

8 (*a*) D. E. Ward and B. F. Kaller, *Tetrahedron Lett.*, 1991, **32**, 843; (*b*) R. Hunter and C. D. Simon, *Tetrahedron Lett.*, 1988, **29**, 2257.

9 G. A. Molander and D. C. Shubert, *Tetrahedron Lett.*, 1986, **27**, 787.

10 (*a*) G. A. Molander and D. C. Shubert, *J. Am. Chem. Soc.*, 1987, **109**, 576; (*b*) see also ref. 4; (*c*) G. A. Molander and D. C. Shubert, *J. Am. Chem. Soc.*, 1987, **109**, 6877.

11 G. Majetich and J. Defauw, *Tetrahedron*, 1988, **44**, 3833.

12 M. Patz and H. Mayr, *Tetrahedron Lett.*, 1993, **34**, 3393.

13 B. M. Trost, D. M. T. Chan and T. N. Nanninga, *Org. Synth.*, 1984, **62**, 266.

14 B. M. Trost and D. Curran, *J. Am. Chem. Soc.*, 1981, **103**, 7380.

15 (*a*) I. Fleming and A. Pearce, *J. Chem. Soc., Perkin Trans.*, 1981, **1**, 251; (*b*) I. Fleming and D. Marchi, Jr., *Synthesis*, 1981, 560.

16 V. J. Jephcote, A. J. Pratt and E. J. Thomas, *J. Chem. Soc., Chem. Commun.*, 1984, 800.

17 N. S. Isaacs, R. L. Marshall and D. J. Young, *Tetrahedron Lett.*, 1992, **33**, 3023.