A Study of the Intramolecular Stille Cross Coupling Reaction of Vinylstannyl Chloroformates: Application to the Synthesis of α-Methylene Lactones

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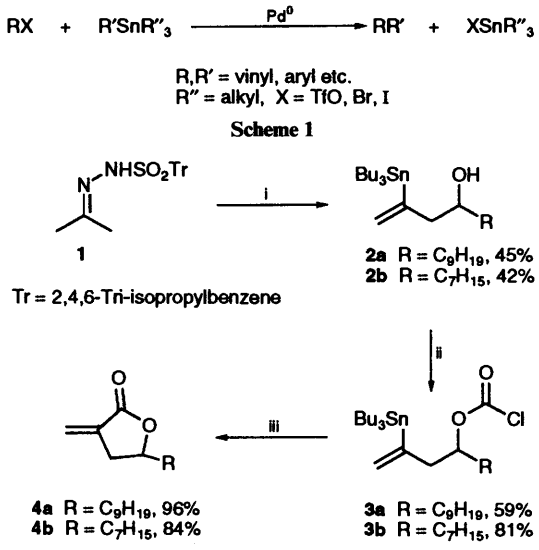
An intramolecular Stille cross coupling of vinylstannyl chloroformates catalysed by *trans*-benzylchlorobis(triphenylphosphine)palladium(II) has been investigated and shown to be useful for the preparation of α-methylene lactones. A novel method for the chloroformylation of alcohols in the presence of vinylstannanes is also described.

The Stille cross coupling reaction[1] (Scheme 1) is a useful carbon–carbon bond-forming reaction. The mild conditions, stereospecific nature of the coupling and increasing availability of organostannanes has led to widespread use of this reaction in organic synthesis.[2] The scope of the reaction has been demonstrated by use of halides, triflates and acid chlorides as the non-tin-containing partner. Prompted by successful reports of palladium-catalyzed macrocyclization[3a] and cyclodimerization of vinylstannylacyl chlorides[3b] we speculated that vinylstannyl chloroformates could react in an analogous fashion.[4] Recently chloroformates have been studied for an intermolecular Stille cross coupling by Jousseaume and coworkers,[5] however, the conditions used are not applicable to an intramolecular Stille cross coupling whereby the vinylstannyl and the chloroformate moieties will be contained within the same molecule. This publication describes our studies on such intramolecular and cyclodimerization Stille cross coupling reactions of vinylstannyl chloroformates from which a synthesis of α-methylene lactones[6] under mild conditions has resulted.

Initially, the assembly of vinylstannyl chloroformates and subsequent palladium-catalyzed cyclization was investigated for 2-(tributylstannyl)alk-1-en-4-ols **2** which were prepared by a modification of the Shapiro reaction[7] using tributylstannyl chloride to quench the so-formed vinyllithium species *in situ*. Chloroformylation of **2** using triphosgene [bis(trichloromethyl)carbonate] as a phosgene alternative[8] in the presence of proton sponge® [1,8-bis(dimethylamino)naphthalene][9] enabled chloroformylation to proceed in good yield. Triphosgene was preferred over other chloroformylating agents owing to the ease of recrystallization from ether–hexane prior to use, thus removing undesirable acidic impurities. The efficient removal of acidic species from the reaction mixture was found to be crucial in avoiding protodestannylation of the vinylstannyl functionality. To this end, at least 1 equiv. of proton sponge was found necessary, enabling precipitation of a hydrochloride salt by-product which was easily removed by filtration on reaction completion. Attempted purification using silica gel chromatography was found to result in protodestannylation, however, purification using the less acidic Florisil® afforded analytically pure vinylstannyl chloroformates **3** in good yield.

The intramolecular cross coupling was facilitated by very slow addition (*ca.* 16 h) of the solution of *trans*-benzylchlorobis(triphenylphosphine)palladium(II) (4.5 mol%) to **3** at 37 °C yielding α-methylene-γ-lactones **4** in excellent yield (Scheme 2). Without slow addition the reaction was incomplete owing to catalyst decomposition whilst use of higher temperatures (65 °C) resulted in facile isomerization of the double bond into the ring. The choice of solvent and catalyst proved very important for intramolecular coupling. For the former 1,2-dichloroethane gave highest yields although THF could also be

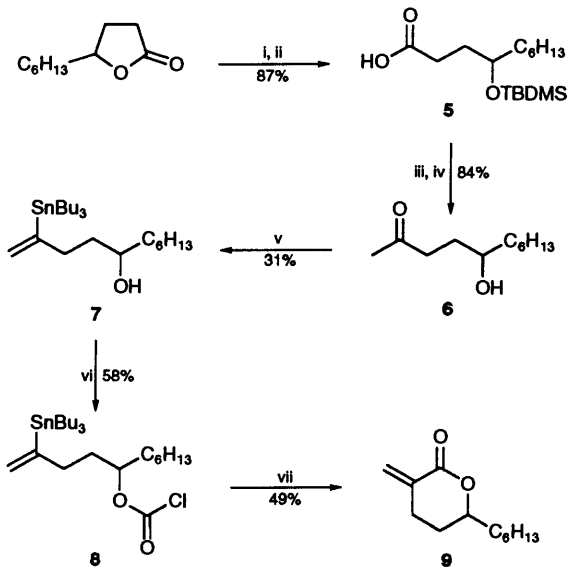


Scheme 2 *Reagents and conditions:* i, BuLi (2.1 equiv.), dimethoxyethane (DME), −78 °C, 30 min then RCHO (1.1 equiv.), −78 °C, 45 min then BuLi (1.1 equiv.), −78 °C to −5 °C, 2 h then Bu_3SnCl (1.2 equiv.), −78 °C to room temp. over 2 h then 16 h at room temp.; ii, proton sponge® (1.1 equiv.), triphosgene (0.34 equiv.), ether, 4 h; iii, $[PhCH_2Pd(PPh_3)_2Cl]$ (4.5 mol%), dichloroethane (DCE), 37 °C, 20 h

used with success. Trifurylphosphine, used to great effect by Farina and Krishnan[10] was also tried as a ligand for the palladium catalyst. However, intramolecular Stille cross coupling proceeded only poorly with incomplete conversion when tetrakis(trifurylphosphine)palladium(II) formed *in situ* at room temperature was employed. It was also found that the instability of this catalyst made it unsuitable for the slow addition, found necessary for high yields of α-methylene lactones when *trans*-benzylchlorobis(triphenylphosphine)palladium(II) was used as catalyst.

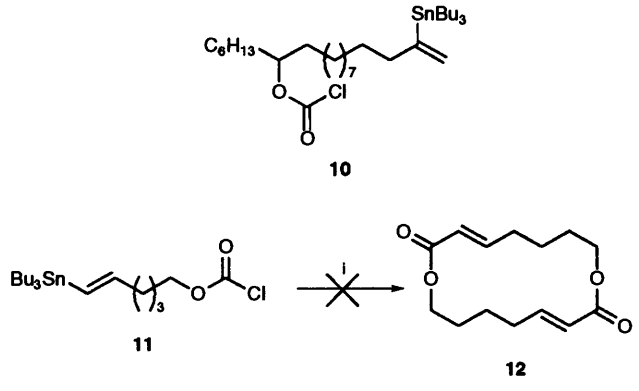
The Stille cross coupling to form five-membered rings is most probably facilitated by ready formation of a six-membered palladium metallocycle. Such considerations led to the expectation of lower efficiencies for the analogous 6- and 7-membered α-methylene lactones. In practice, intramolecular coupling could be extended to 6-membered but not to 7-membered α-methylene lactones (Scheme 3).

The vinylstannyl alcohol **7** was obtained from (±)-γ-decanolactone[11] using standard methods[12] and Shapiro chemistry. Again the use of proton sponge® and triphosgene proved successful conditions for chloroformylation without protodestannylation and 6-hexyl-3-methylenetetrahydropyran-2-one **9** was obtained only when very slow addition of the catalytic solution was conducted at room temperature.



Scheme 3 *Reagents and conditions:* i, LiOH·H_2O, dioxane–H_2O, 72 h then *tert*-butyldimethylsilyl chloride (TBDMSCl), imidazole, dimethylformamide (DMF), 20 h; ii, K_2CO_3, MeOH–H_2O–THF, 2 h then 1 mol dm^{-3} $KHSO_4$; iii, MeLi, THF, 0 °C, 2 h then trimethylsilyl chloride (TMSCl), 0 °C to room temp. then 1 mol dm^{-3} HCl, 30 min; iv, tetrabutylammonium fluoride (TBAF), THF, 2 h; v, 2,4,6-$TrSO_2NHNH_2$, Dowex-50, 4 Å mol. sieves, ether, 30 min then BuLi (3.4 equiv.), DME, −78 °C to −5 °C, 3 h then Bu_3SnCl (1.4 equiv.), −78 °C to room temp. over 2 h then 16 h at room temp.; vi, proton sponge® (1.1 equiv.), triphosgene (0.34 equiv.), ether, 4 h; vii, [$PhCH_2Pd(PPh_3)_2Cl$] (4.5 mol%), DCE, room temp., 92 h

Finally, 18-(tributylstannyl)nondec-18-en 7-yl chloroformate **10**, and (E)-6-(tributylstannyl)hex-5-enyl chloroformate **11** were synthesised and investigated for palladium-catalyzed macrocyclization and cyclodimerization, respectively. Disappointingly, compound **10** gave no macrocyclization products and only traces of 1,9-dioxahexadec-3,11-diene-2,10-dione **12** under a variety of reaction conditions (Scheme 4).



Scheme 4 *Reagents and conditions:* i, [$PhCH_2Pd(PPh_3)_2Cl$] (7 mol%), toluene, 100 °C, 20 h

In summary, we have demonstrated that vinylstannyl chloroformates undergo intramolecular Stille cross coupling using the catalyst *trans*-benzylchlorobis(triphenylphosphine)palladium-(II) to provide a novel route to α-methylene lactones. An effective method for the chloroformylation of vinylstannyl alcohols has, likewise, been reported.

Experimental

General Details.—^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz, respectively, on a Varian Gemini 200 spectrometer using $CDCl_3$ as solvent, referencing to the residual solvent peak. DEPT techniques were employed to determine the number of hydrogens attached to each carbon. *J* Values are given in Hz to the nearest 0.5 Hz. Elemental analyses were carried out within the Dyson Perrins Laboratory. IR spectra were recorded as thin films using a Perkin-Elmer 1750 Fourier Transform spectrometer. Low resolution mass spectra were recorded on a V.G. Micromass ZAB IF, V.G. Masslab 20-250 or a V.G. TRIO 1 (GCMS) spectrometer, with only molecular ions (M^+), fractions of molecular ions and major peaks being reported. Progress of all reactions were followed by TLC analysis using Kieselgel 60 F_{254} plates which were visualised by UV fluorescence (λ_{max} = 254 nm), or by staining with 10%(w/v) ammonium molybdate in 2 mol dm^{-3} sulphuric acid followed by heat. R_F Values are quoted to the nearest 0.05. All solvents were distilled before use. Anhydrous 1,2-dichloroethane and 1,2-dimethoxyethane were obtained by stirring over calcium hydride for 24 h followed by distillation under argon. Anhydrous diethyl ether, referred to as ether, and anhydrous THF were obtained by distillation from sodium/benzophenone ketal under nitrogen. LP refers to the fraction of light petroleum boiling in the range 30–40 °C.

General Procedure for Preparation of 2-(*Tributylstannyl*)*alk*-1-*en*-4-*ols*.—2-*Tributylstannyltridec*-1-*en*-4-*ol* **2a**. To a stirred solution of acetone 2,4,6-triisopropylbenzenesulfonylhydrazone **1**[7] (3.38 g, 10.0 mmol) in 1,2-dimethoxyethane (30 cm^3), under an inert atmosphere of argon at −78 °C was added, dropwise, butyllithium(1.33 mol dm^{-3} in hexane; 15.8 cm^3, 21.0 mmol). The resulting yellow solution was stirred for 30 min after which decanal (2.03 g, 11.0 mmol) was added to form a clear solution which was stirred for a further 45 min at −78 °C. Addition of butyllithium (1.33 mol dm^{-3}; 8.30 cm^3, 11.0 mmol) to the mixture produced a yellow solution which was allowed to warm to −5 °C over 2 h with evolution of nitrogen gas. After recooling of the mixture to −78 °C the reaction was quenched with tributylstannyl chloride (3.91 g, 12.0 mmol) and the resulting pale green solution stirred for 18 h; during the first 2 h it was allowed to warm slowly to room temperature. The solution was then poured into LP (50 cm^3) and washed sequentially with acetonitrile (30 cm^3)–water (15 cm^3) and acetonitrile (30 cm^3). The LP layer was separated, dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a colourless oil, flash chromatography (SiO_2, LP:ether; 20:1; 2:1, gradient elution) of which afforded the *title compound* **2a** as a colourless oil (2.13 g, 45%); R_F 0.4, LP–ether, 19:1) (Found: C, 61.8; H, 10.8. $C_{25}H_{52}OSn$ requires C, 61.61; H, 10.75%); ν_{max}/cm^{-1} 3400–3200br m (OH), 2956s (CH), 2927s (CH) and 1070w (C-O); δ_H(200 MHz; $CDCl_3$) 0.87–1.05 (18 H, m), 1.17–1.20 (28 H, m), 2.24 (1 H, dd, ^2J 13.5, ^3J 9, C=CCH_aH_b), 2.54 (1 H, dd, ^2J 13.5, ^4J 2.5 C=CCH_aH_b), 3.48–3.63 (1 H, m, CHOH), 5.32 (1 H, d, ^4J 2.5, *Z*-SnC=CH_aH_b, $^3J_{Sn-H}$ 32), 5.80 (1 H, s, *E*-SnC=CH_aH_b, $^3J_{Sn-H}$ 66); δ_C(50 MHz; $CDCl_3$) 9.55 (SnCH_2), 13.53, 13.97 (Me), 22.57, 25.65, 27.30, 27.86, 28.80, 28.99, 29.24, 29.53, 31.82 (CH_2), 36.80 ($C_8H_{17}CH_2$), 49.62 (C=CCH_2), 69.89 (CHOH), 129.02 (SnC=*C*) and 152.84 (Sn*C*=C); *m/z* (CI^+, NH_3) 487 [1.5%, M^+ (^{120}Sn)-H], 485 [1.2, M^+ (^{118}Sn)-H], 483 [0.4, M^+ (^{116}Sn)-H], 431 [27, M^+ (^{120}Sn)-Bu], 429 [25, M^+ (^{118}Sn)-Bu] and 427 [12, M^+ (^{116}Sn)-Bu] and 306 [100].

2-*Tributylstannylundec*-1-*en*-4-*ol* **2b**.—This compound was obtained in 42% yield from **1** (7.8 mmol scale; R_F 0.3 (LP–ether, 19:1) (Found: C, 59.95; H, 10.6. $C_{23}H_{48}OSn$ requires C, 60.14; H, 10.53%); ν_{max}/cm^{-1} 3436br m (OH), 2927s (CH) and 1073w (C-O); δ_H(200 MHz; $CDCl_3$) 0.76–1.14 (18 H, m), 1.19–1.71 (24 H, m), 2.25 (1 H, dd, ^2J 12, ^3J 8, C=CCH_aH_b), 2.51 (1 H, dd, ^2J 12, ^4J 2.5, C=CCH_aH_b), 3.51–3.55 (1 H, m, CHOH), 5.33 (1 H, d,

^4J 2.5, Z-SnC=CH_aH_b), 5.80 (1 H, br s, E-SnC=CH_aH_b); δ_C(50 MHz; $CDCl_3$) 9.55 ($SnCH_2$), 13.51, 13.94 (Me), 22.54, 25.64, 27.86, 28.99, 29.25, 29.54, 31.75 (CH_2), 36.81 (CH_2CH_2CHOH), 49.61 (C=CCH_2), 69.91 (CHOH), 129.00 (SnC=C) and 152.85 (SnC=C); *m/z* (CI^+, NH_3) 403 [100%, M^+ (^{120}Sn)-Bu], 401 [92, M^+ (^{118}Sn)-Bu], 399 [51, M^+ (^{116}Sn)-Bu], 251 [26] and 177 [31].

*General Procedure for Chloroformylation of Vinylstannyl Alcohols.**—*2-(Tributylstannyl)tridec-1-en-4-yl chloroformate* **3a**. To a stirred solution of the tridecenol **2a** (604 mg, 1.24 mmol) in dry ether (5 cm^3), under an inert atmosphere or argon, was added proton sponge® (300 mg, 1.40 mmol). Triphosgene (125 mg, 0.42 mmol) freshly recrystallized from hexane–ether was added in dry ether (2 cm^3) to the mixture to give, within minutes, a yellow solution. After 4 h the solution was concentrated under reduced pressure to afford a yellow oil, flash chromatography (Florisil®-200 mesh, 20 g, LP) of which afforded the *title compound* **3a** as a colourless oil (400 mg, 59%), R_F 0.95 (LP–ether, 19:1) (Found: C, 56.9; H, 9.3. $C_{26}H_{51}ClO_2Sn$ requires C, 56.80; H, 9.35%); ν_{max}/cm^{-1} 2957s (CH), 2927s (CH), 2855s (CH), 1776s (C=O), 1160s, ($ClCO_2$) and 1074w (C–O); δ_H(200 MHz; $CDCl_3$) 0.78–1.11 (18 H, m), 1.18–1.65 (28 H, m), 2.52 (1 H, dd, ^2J 14, ^3J 6, C=CCH_aH_b), 2.64 (1 H, dd, ^2J 14, ^3J 6, C=CCH_aH_b), 4.93 (1 H, quin., ^3J 6 CHO), 5.29 (1 H, s, Z-SnC=CH_aH_b, $^3J_{Sn-H}$ 34) and 5.79 (1 H, s, E-SnC=CH_aH_b, $^3J_{Sn-H}$ 68); δ_C(50 MHz; $CDCl_3$) 9.48 ($SnCH_2$), 13.54, 13.98 (Me), 22.57, 25.05, 27.30, 27.84, 28.76, 28.95, 29.19, 29.36, 31.79, 33.38 (CH_2), 45.36 (C=CCH_2), 83.65 (CHO), 129.69 (SnC=C), 149.42 (SnC=C) and 150.36 ($ClCO_2$); *m/z* (CI^+, NH_3) 413 [28%, M^+ (^{120}Sn)-(Bu, $ClCO_2H$)], 411 [25, M^+ (^{118}Sn)-(Bu, $ClCO_2H$)], 409 [12, M^+ (^{116}Sn)-(Bu, $ClCO_2H$)] and 269 [100].

2-*(Tributylstannyl)undec-1-en-4-yl chloroformate* **3b**. This compound was obtained in 81% yield from **2b**, (1.3 mmol scale), R_F 0.95 (LP) (Found: C, 55.5; H, 9.0. $C_{24}H_{47}ClO_2Sn$ requires C, 55.25; H, 9.06%); ν_{max}/cm^{-1} 2957s (CH), 2927s (CH), 1775s (C=O) and 1162s ($ClCO_2$); δ_H(200 MHz; $CDCl_3$) 0.77–1.06 (18 H, m), 1.20–1.65 (24 H, m), 2.51 (1 H, dd, ^2J 14, ^3J 7, C=CCH_aH_b), 2.63 (1 H, dd, ^2J 14, ^3J 7, C=CCH_aH_b), 4.92 (1 H, quin., ^3J 7, CHO), 5.28 (1 H, s, Z-SnC=CH_aH_b, $^3J_{Sn-H}$ 30) and 5.78 (1 H, s, E-SnC=CH_aH_b, $^3J_{Sn-H}$ 63.5); δ_C(50 MHz; $CDCl_3$) 9.48 ($SnCH_2$), 13.51, 13.91 (Me), 22.47, 24.46, 25.05, 27.27, 28.95, 29.25, 31.62, 33.39 (CH_2), 45.33 (C=CCH_2), 83.65 (CHO), 129.67 (SnC=C), 149.45 (SnC=C) and 150.37 ($ClCO_2$); *m/z* (CI^+, NH_3) 385 [22%, M^+ (^{120}Sn)-(Bu, $ClCO_2H$)], 269 (100), 267 (81), 213 (22) and 177 (48).

2-*(Tributylstannyl)undec-1-en-5-yl chloroformate* **8**. This compound was obtained in 58% yield from **7** (0.4 mmol scale), R_F 0.9, (LP–ether, 19:1); ν_{max}/cm^{-1} 2957s (CH), 2927s (CH), 2856s (CH), 1777s (C=O) and 1164s ($ClCO_2$); δ_H(200 MHz; $CDCl_3$) 0.84–1.07 (18 H, m), 1.34–1.85 (24 H, m), 2.26–2.44 (2 H, m, C=CCH_2), 4.93 (1 H, quin., ^3J 6, CHO), 5.17 (1 H, s, Z-SnC=CH_aH_b, $^3J_{Sn-H}$ 32) and 5.71 (1 H, s, E-SnC=CH_aH_b, $^3J_{Sn-H}$ 61); δ_C(50 MHz; $CDCl_3$) 9.40 ($SnCH_2$), 13.54, 13.88 (Me), 22.40, 24.87, 27.28, 28.90, 29.00, 31.52, 33.48, 33.68 (CH_2), 36.40 ($C_5H_{11}CH_2$), 84.25 (CHO), 126.05 (SnC=C), 150.47 ($ClCO_2$) and 153.79 (SnC=C); *m/z* (CI^+, NH_3) 385 [100%, M^+ (^{120}Sn)-(Bu, $ClCO_2H$)], 383 [72, M^+ (^{118}Sn)-(Bu, $ClCO_2H$)], 381 [45, M^+ (^{116}Sn)-(Bu, $ClCO_2H$)], 329 (14), 327 (12), 325 (8), 269 (54) and 177 (46).

General Procedure for Intramolecular Stille Cross Coupling to provide **4a** *and* **4b**.—*3-Methylene-5-nonyltetrahydrofuran-2-one* **4a**. To a stirred solution of the chloroformate **3a** (209 mg, 0.38 mmol) in 1,2-dichloroethane (4 cm^3) at 37 °C, under an inert atmosphere of argon, was slowly added over 16 h *trans*-benzyl(chloro)bis(triphenylphosphine)palladium(II) (13 mg, 4.5 mol%) in 1,2-dichloroethane (5 cm^3). The resulting black solution was stirred for a further 4 h after which it was evaporated under reduced pressure and the residue transferred to a flash silica column, washing with LP (500 cm^3). Flash chromatography (SiO_2, LP–ether, 3:1) afforded the *title compound* **4a** as a colourless oil (82 mg, 96%); R_F 0.35 (LP–ether, 3:1) (Found: C, 74.9; H, 10.8. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%); ν_{max}/cm^{-1} 2927s (CH), 2856s (CH), 1767s (C=O) and 1666m (C=C); δ_H(200 MHz; $CDCl_3$) 0.88 (3 H, t, ^3J 6.5, CH_3), 1.07–1.77 (16 H, m, $[CH_2]_8$), 2.50–2.65 (1 H, m, 4-CH_aH_b), 2.98–3.13 (1 H, m, 4-CH_aH_b), 4.45–4.59 (1 H, m, CHO), 5.63 (1 H, t, ^4J 2.5, C=CH_aH_b), 6.23 (1 H, t, ^4J 3, C=CH_aH_b); δ_C(50 MHz; $CDCl_3$) 13.95 (CH_3), 22.53, 24.73, 26.72, 27.71, 29.17, 29.34, 31.75 (CH_2), 33.43, 36.19 (4-CH_2, $C_8H_{17}CH_2$), 77.67 (CHO), 122.05 (C=CH_2), 135.00 (C=CH_2) and 170.74 (C=O); *m/z* (CI^+, NH_3) 242 (100%, MNH_4^+), 225 (41, MH^+) and 140 (3).

5-*Heptyl-3-methylenetetrahydrofuran-2-one* **4b**. This compound was obtained in 84% yield from **3b** (0.6 mmol scale); R_F 0.3 (LP–ether, 3:1) (Found: C, 73.1; H, 10.7. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%); ν_{max}/cm^{-1} 2928s (CH), 2857s (CH), 1765s (C=O) and 1666m (C=C); δ_H(200 MHz; $CDCl_3$) 0.78–0.90 (3 H, m, CH_3), 1.08–1.76 [12 H, m, $(CH_2)_6$] 2.50–2.64 (1 H, m, 4-CH_aH_b), 2.97–3.13 (1 H, m, 4-CH_aH_b), 4.44–4.58 (1 H, m, CHO), 5.62 (1 H, t, ^4J 2.5, C=CH_aH_b) and 6.22 (1 H, t, ^4J 3, C=CH_aH_b); δ_C(50 MHz; $CDCl_3$) 13.91 (CH_3), 24.46, 24.72, 29.00, 29.13, 31.60 (CH_2), 33.45, 36.18 (4-CH_2, CH_2CHO), 77.64 (CHO), 122.04 (C=CH_2), 135.00 (C=CH_2) and 170.73 (C=O); *m/z* (CI^+, NH_3) 214 (12%, MNH_4^+), 197 (70, MH^+), 151 (26), 140 (15) and 97 (100, $M^+ - C_7H_{15}$).

4-tert-*Butyldimethylsilyloxydecanoic Acid* **5**.—To a stirred solution of (±)-γ-decanolactone (3.40 g, 20.0 mmol) in 1,4-dioxane (40 cm^3)–water (20 cm^3), under an inert atmosphere of argon, was added lithium hydroxide monohydrate (839 mg, 20.0 mmol). After dissolution of the latter (30 min) the solution was stirred for 72 h and then concentrated under reduced pressure to yield lithium 4-hydroxydecanoate as a white solid in quantitative yield (3.88 g) after freeze drying.

To a stirred solution of lithium 4-hydroxydecanoate (1.99 g, 10.2 mmol) in DMF (20 cm^3) was added TBDMSCl (3.39 g, 22.6 mmol) and imidazole (2.09 g, 30.7 mmol). The resulting yellow solution was stirred for 20 h and then extracted with ethylacetate (20 cm^3). The extract was washed with water (2 × 60 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield tert-*butyldimethylsilyl* 4-(tert-*butyldimethylsilyloxy)decanoate* as a colourless oil (4.15 g, 97%), R_F 0.7, LP–ether, 1:1) (Found: C, 63.2; H, 11.5. $C_{22}H_{48}O_3Si_2$ requires C, 63.40; H, 11.61%); ν_{max}/cm^{-1} 2957s (CH), 2931s (CH), 2859s (CH), 1719s (C=O), 1255m ($SiMe_2$) and 1177m (C–O); δ_H(200 MHz; $CDCl_3$) 0.05, 0.27 [12 H, 2 × s, $Si(CH_3)_2$], 0.89, 0.93 [18 H, 2 × s, $SiC(CH_3)_3$], 0.86–0.98 (3 H, m, CH_3CH_2), 1.21–1.78 [12 H, m, $(CH_2)_5$, CH_2], 2.38 (2 H, t, ^3J 7.5, CH_2CO_2) and 3.70–3.73 (1 H, m, CHO); δ_C(50 MHz; $CDCl_3$) −4.62, −5.03 [2 × $Si(CH_3)_2$], 13.94 (CH_3CH_2), 17.44, 17.95 (2 × $SiCMe_3$), 25.42, 25.76 [2 × $SiC(CH_3)_3$], 22.49, 25.05, 29.37, 31.54, 31.74, 36.87, 37.02 (CH_2), 71.16 (CHO) and 174.86 (CO_2); *m/z* (CI^+, NH_3) 417 (100, MH^+), 359 (20, M^+ − Bu), 303 (32), 285 (52, $M^+ - OSiMe_2Bu^t$), 245 (9) and 171 (5).

To a stirred solution of the preceding ester (2.99 g, 7.17 mmol) in MeOH (40 cm^3)–water (10 cm^3)–THF (10 cm^3), under an inert atmosphere of argon, was added potassium carbonate (2.00 g, 14.5 mmol). After 2 h the solution was concentrated

* The chloroformylation procedure has also been applied successfully to 2-(tributylstannyl)alk-1-en-6- and -13-ols (*e.g.* to give **10**) and 1-(tributylstannyl)alk-1-en-6-ols (*e.g.* to give **11**).

under reduced pressure to *ca.* 20 cm^3, diluted with ether (60 cm^3) and acidified with 1 mol dm^{-3} aq. $KHSO_4$. The solution was extracted with ether (2 × 30 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the *title compound* **5** as a colourless oil (1.95 g, 90%); (R_F 0.65, LP–ether, 10:1); ν_{max}/cm^{-1} 3390–2320br s (OH), 2931s (CH), 1713s (C=O), 1256m ($SiMe_2$) and 1083m (C–O); δ_H(200 MHz; $CDCl_3$) 0.06 [6 H, s, $Si(CH_3)_2$], 0.81–0.93 (3 H, m, CH_3CH_2), 0.90 [9 H, s, $C(CH_3)_3$], 1.19–1.52 [10 H, m, $(CH_2)_5$], 1.63–1.87 (2 H, m, $CH_2CH_2CO_2$), 2.44 (2 H, t, ^3J 7.5, CH_2CO_2) and 3.73 (1 H, quin., ^3J 5, CHO); δ_C(50 MHz; $CDCl_3$) −4.65 [$Si(CH_3)_2$], 13.92 (CH_3CH_2), 17.92 (CMe_3), 25.74 [$C(CH_3)_3$], 22.48, 25.02, 29.34, 29.74, 31.23, 31.73, 36.87 (CH_2), 71.11 (CHOSi) and 180.78 (CO_2); *m/z* (CI^+, NH_3) 303 (100, MH^+), 285 (5, M^+ − OH), 245 (15, M^+ − Bu) and 171 (15).

5-Hydroxyundecan-2-one **6**.—To a stirred solution of the acid **5** (1.20 g, 4.00 mmol) in THF (30 cm^3), under an inert atmosphere of argon, was added methyllithium (0.97 mol dm^{-3} in ether; 16.5 cm^3, 16.0 mmol), at 0 °C. After 2 h TMSCl (10.0 cm^3, 80.0 mmol) was added to the mixture which was then allowed to warm to room temperature. It was then treated with 1 mol dm^{-3} HCl (15 cm^3) and the resulting two-phase system stirred for 30 min. The mixture was extracted with ether (3 × 25 cm^3) and the combined extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield 5-*tert*-*butydimethylsilyloxyundecan-2-one* as a colourless oil (1.08 g, 91%); R_F 0.7 (LP–ether, 1:1) (Found: C, 67.8; H, 12.4. $C_{17}H_{36}O_2Si$ requires C, 67.94; H, 12.07%); ν_{max}/cm^{-1} 2956s (CH), 2930s (CH), 1712s (C=O), 1256m ($SiMe_2$) and 1082m (C–O); δ_H(200 MHz; $CDCl_3$) 0.04 [6 H, s, $Si(CH_3)_2$], 0.85–0.97 (3 H, m, CH_3CH_2), 0.89 [9 H, s, $C(CH_3)_3$], 1.20–1.38 [8 H, m, $(CH_2)_4$], 1.58–1.79 (4 H, m, CH_2CHOCH_2), 2.15 (3 H, s, CH_3CO), 2.49 (2 H, t, ^3J 8, CH_2C=O) and 3.68 (1 H, quin., ^3J 5, CHO); δ_C(50 MHz; $CDCl_3$) −4.65 [$Si(CH_3)_2$], 13.92 (CH_3CH_2), 17.92 (CMe_3), 25.74 [$C(CH_3)_3$], 22.47, 25.09, 29.35, 30.31, 31.75, 36.98, 39.18 (CH_2), 29.82 (CH_3C=O), 71.20 (CHOSi) and 209.70 (C=O); *m/z* (CI^+, NH_3) 186 (7%, MH^+ − $SiMe_2Bu^t$] and 170 (100, MH^+ − $OSiMe_2Bu^t$).

To a stirred solution of the foregoing ketone (992 mg, 3.31 mmol) in THF (10 cm^3), under an inert atmosphere of argon, was added TBAF (1.1 mol dm^{-3} in THF; 3.30 cm^3, 3.60 mmol). The resulting orange solution was stirred for 2 h then concentrated under reduced pressure to yield an orange oil. Flash chromatography (SiO_2, LP–ether; 3:1→1:3, gradient elution) afforded the *title ketone* **6** as a colourless oil (567 mg, 92%), R_F 0.35 (LP–ether, 1:3) (Found: C, 71.0; H, 12.1. $C_{11}H_{22}O_2$ requires C, 70.92; H, 11.90%); ν_{max}/cm^{-1} 3700–3100br s (OH), 2931s (CH), 2858s (CH), 1713s (C=O) and 1164m (C–O); δ_H(200 MHz; $CDCl_3$) 0.88 (3 H, t, ^3J 6.5, CH_3CH_2), 1.21–2.14 [12 H, m, $CH_2CH(OH)(CH_2)_5$], 2.18 (3 H, s, CH_3C=O), 2.61 (2 H, t ^3J 7, CH_2C=O) and 3.56–3.64 (1 H, m, CHOH); δ_C(50 MHz; $CDCl_3$) 13.92 (CH_3CH_2), 22.47, 25.49, 29.18, 30.67, 31.71, 37.67, 40.02 (CH_2), 29.93 (CH_3CO), 71.39 (CHOH) and 208.54 (C=O); *m/z* (CI^+, NH_3) 187 (8%, MH^+), 186 (100, M^+), 142 (51) and 100 (15).

2-Tributylstannyldec-1-en-5-ol **7**.—To a stirred solution of the *ketone* **6** (400 mg, 2.15 mmol) in dry ether (6 cm^3), under an inert atmosphere of argon, was added 2,4,6-triisopropylbenzenesulfonohydrazide (641 mg, 2.15 mmol), 4 Å molecular sieves (1 g) and Dowex 50 (50 mg). The resulting grey suspension was stirred for 30 min, filtered and concentrated under reduced pressure to yield an orange oil. Benzene (3 × 5 cm^3) was added to the oil and traces of water removed by sequential azeotropic concentration under reduced pressure. The brown residue was dissolved in freshly distilled 1,2-dimethoxyethane (10 cm^3) and the solution cooled to −78 °C. This, upon dropwise addition of butyllithium (1.45 mol dm^{-3} in hexane; 5.00 cm^3, 7.25 mmol) to it, afforded an orange solution which was allowed to warm to −5 °C over 3 h with evolution of nitrogen gas. After recooling of the solution to −78 °C, tributylstannyl chloride (980 mg, 3.01 mmol), was added to it and the resulting yellow solution allowed to warm to room temperature over 2 h; it was then stirred for a further 16 h. The solution was poured into LP (40 cm^3) and washed sequentially with acetonitrile (20 cm^3)–water (10 cm^3) and acetonitrile (20 cm^3). The LP layer was separated, dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield a colourless oil, flash chromatography (SiO_2, LP–ether; 50:1→1:1, gradient elution) of which afforded the title compound **7** as a colourless oil (305 mg, 31%); R_F 0.05 (LP–ether, 19:1) (Found: C, 60.45; H, 10.8. $C_{23}H_{48}OSn$ requires C, 60.14; H, 10.53%); ν_{max}/cm^{-1} 3580–3120br m (OH), 2958s (CH), 2928s (CH), 2858m (CH) and 1159w (C–O); δ_H(200 MHz; $CDCl_3$) 0.85–0.96 (18 H, m), 1.26–1.63 (24 H, m), 2.24–2.52 (2 H, m, $C{=}CCH_2$), 3.59–3.64 (1 H, m, CHOH), 5.15 (1 H, d, ^4J 2.5, *Z*-SnC=CH_aH_b, $^3J_{Sn-H}$ 32) and 5.74 (1 H, d, ^4J 2.5, *E*-SnC=CH_aH_b, $^3J_{Sn-H}$ 70); δ_C(50 MHz; $CDCl_3$) 9.43 ($SnCH_2$), 13.55, 13.94 (CH_3), 22.50, 25.49, 27.30, 29.02, 29.27, 31.75, 37.06, 37.39 (CH_2), 71.36 (CHOH), 125.32 (SnC=*C*) and 155.57 (Sn*C*=C); *m/z* (CI^+, NH_3) 461 [1.4%, MH^+ (^{120}Sn)], 459 [1.2, MH^+ (^{118}Sn)], 457 [0.7, MH^+ (^{116}Sn)], 403 [30, M^+ (^{120}Sn)-Bu], 401 [25, M^+ (^{118}Sn)-Bu], 399 [14, M^+ (^{116}Sn)-Bu], 308 (100), 306 (78), 291 (33) and 169 (35).

6-Hexyl-3-methylenetetrahydropyran-2-one **9**.—To a stirred solution of the chloroformate **8** (118 mg, 0.23 mmol) in 1,2-dichloroethane (5 cm^3), under an inert atmosphere of argon, was added slowly over 24 h *trans*-benzyl(chloro)bis(triphenylphosphine)palladium(II) (3 mg, 1.5 mol%) in 1,2-dichloroethane (3 cm^3). Solvent was removed from the mixture under reduced pressure and ^1H NMR analysis of the residue revealed that **9** had been formed in *ca.* 35% yield. The residue was then dissolved in 1,2-dichloroethane (8 cm^3) and further catalyst (5 mg, 3 mol%) was added to the solution. After 68 h the mixture was evaporated under reduced pressure and the residue transferred to a flash silica column, washing with LP (500 cm^3). Flash chromatography (SiO_2, LP–ether, 7:1) followed by preparative layer chromatography (two developments with LP–ether, 7:1) afforded the *title compound* **9** (22 mg, 49%); R_F 0.2 (LP–ether, 7:1); ν_{max}/cm^{-1} 2928s (CH), 2857s (CH), 1719s (C=O) and 1624w (C=C); δ_H(200 MHz; $CDCl_3$) 0.89 (3 H, t, ^3J 7, CH_3), 1.11–1.77 [11 H, m, 5-CH_aH_b, $(CH_2)_5$], 1.90–2.01 (1 H, m, 5-CH_aH_b), 2.56–2.70 (2 H, m, 4-CH_2), 4.20–4.35 (1 H, m, CHO), 5.56 (1 H, d, ^4J 2, C=CH_aH_b) and 6.42 (1 H, br s, C=CH_aH_b); δ_C(50 MHz; $CDCl_3$) 13.91 (CH_3), 24.43, 24.72, 27.10, 28.11, 28.97, 31.58, 35.53 (CH_2), 80.82 (CHO), 126.06 ($C{=}CH_2$), 134.13 ($C{=}CH_2$) and 166.30 (C=O); *m/z* (CI^+, NH_3) 214 (51%, MNH_4^+), 197 (100, MH^+), 151 (6) and 128 (5).

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