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Scope of the Chromium(II)-Mediated Synthesis of *E*-Alkenylstannanes from Aldehydes and $Bu_3SnCHBr_2$

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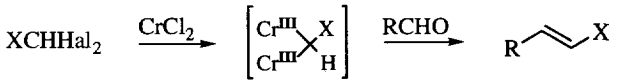
Abstract: *The synthesis of E-alkenylstannanes from aldehydes and a mixture of $Bu_3SnCHBr_2$, LiI and $CrCl_2$ is described. A mechanism is proposed to account for the alkene geometry in chromium(II)-mediated alkene synthesis which involves stereoselective addition by a gem-dichromium reagent to an aldehyde followed by a stereospecific elimination step.*

Alkenylstannanes are finding increasing application in organic synthesis, where they function as excellent substrates for transferring the alkenyl group to electrophiles, normally with retention of alkene geometry.[1] This carbon-carbon bond forming process has been effected *via* transmetallation, either to alkenyllithiums using alkyllithiums,[1] or more recently, for example, directly to alkenylcuprates using higher order alkylcuprates.[2] A considerable amount of research has focused on the palladium-catalysed cross-coupling reactions of alkenylstannanes in particular, because most classes of organo halide or triflate couple efficiently and high functional group tolerance is observed in both the alkenylstannane and the electrophilic partner during the coupling.[3] Alkenylstannanes are usually prepared from alkynes, either by hydrostannylation or stannylmetallation.[1,4] The conversion of carbonyl compounds into predominantly *E*-2-substituted-1-alkenylstannanes (*E*:*Z* ~10 -100:1) has recently been achieved from aldehydes by sequential treatment with Bu_3SnLi then Ph_3PI_2, followed by elimination of HI from the resulting α-iodostannanes using DBU.[5] Direct one-carbon homologation of aldehydes to alkenylstannanes by a Peterson reaction has been examined using $KCHSiMe_3SnBu_3$, which gave the alkenylstannane from benzaldehyde - but as a mixture of isomers in low yield (35%, *E*:*Z* 55:45).[6] Enolisable carbonyl compounds were deprotonated by $KCHSiMe_3SnBu_3$.[6] Horner-type reaction of benzaldehyde with $LiPh_2P(O)CHSnPh_3$ results in formation of the phosphoryl-substituted alkene (92%).[7]

A method for direct homologation of aldehydes to alkenylstannanes which proceeds with high chemo- and stereo-selectivity would be desirable, since it would provide simple access to highly functionalised stannanes and enhance the range of stannane partners available for palladium-catalysed cross-coupling reactions. *Gem*-dichromium reagents (Eq. 1, X = Hal, alkyl, SPh, $SiMe_3$), derived from *gem*-dihalides, have recently been developed to homologate aldehydes to predominantly (X = Hal, alkyl, SPh) or exclusively (X = $SiMe_3$) *E*-alkenes under very mild conditions.[8]



(1)

In this paper we detail our studies in the development and scope of a method for the synthesis of *E*-alkenylstannanes by chromium-mediated one-carbon homologation of aldehydes (Eq. 1, X = $SnBu_3$).[9] In order to examine this chemistry we first required an efficient synthesis of a suitable stannyl-substituted dihalide. Consideration of the stability, handling and storage problems of stannyl-substituted diiodides,[10] as well as the toxicity and volatility of trimethylstannyl-substituted materials,[1] together with the greater reactivity of *gem*-dibromides over *gem*-dichlorides in chromium-mediated alkene synthesis,[11] led us to study $Bu_3SnCHBr_2$. $Me_3SnCHBr_2$ has been prepared (41%) by a low temperature reaction between $Br_2CHMgCl$ (itself prepared from $CHBr_3$ and Pr^iMgCl) and Me_3SnBr.[12] However, rather than adapt this chemistry, modification of a procedure for the synthesis of $Br_2CHSiMe_3$[13] resulted in a highly satisfactory preparation of $Br_2CHSnBu_3$ (Eq. 2).

$$CH_2Br_2 \xrightarrow[THF/Et_2O,\ -90\ ^\circ C]{LDA} [LiCHBr_2] \xrightarrow[THF/Et_2O,\ -90\ ^\circ C]{Bu_3SnCl} Bu_3SnCHBr_2 \qquad (2)$$

Attempted purification of the crude $Bu_3SnCHBr_2$ by distillation (b.p. 120 °C, 0.03 mmHg) gave $Bu_3SnCHBr_2$ contaminated with Bu_3SnCH_2Br[14] (90:10 by ^1H NMR integration of $Bu_3SnCHBr_2$: Bu_3SnCH_2Br), which was not present in the crude material. However, purification of the crude $Bu_3SnCHBr_2$ by flash chromatography gave $Bu_3SnCHBr_2$ as the first eluted product in excellent yields (~90% on scales from 0.5 g to 20 g of $Bu_3SnCHBr_2$), followed by $Bu_2Sn(CHBr_2)_2$ (3%). The latter may have arisen on aqueous work-up from the *ate* complex $Bu_3Sn(CHBr_2)_2Li$ which could stablise excess $LiCHBr_2$. Reversible *ate* complex formation during addition of Bu_3SnCl, rather than deprotonation of $Bu_3SnCHBr_2$ by $LiCHBr_2$, would also explain why $(Bu_3Sn)_2CBr_2$ was not detected (*c.f.* $(Me_3Si)_2CBr_2$ in the preparation of $Me_3SiCHBr_2$)[13] and thus the high yields of $Bu_3SnCHBr_2$.

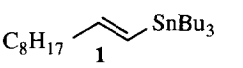
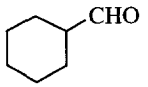
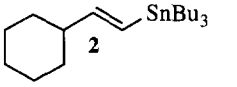
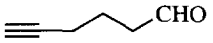
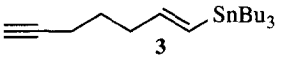
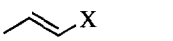
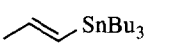
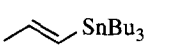
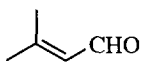
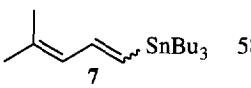
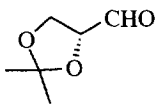
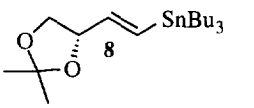
Initial experiments with $Bu_3SnCHBr_2$ were conducted using benzaldehyde. $Bu_3SnCHBr_2$ was reduced very slowly by $CrCl_2$ in THF at 25 °C, and unreacted $Bu_3SnCHBr_2$, Bu_3SnCH_2Br and the *E*-alkenylstannane[6] were observed after 24 h. The reaction was fast in DMF at 25 °C (15 min.), but the *Z*-isomer[6] could be detected (*E*:*Z* 87:13, by ^1H NMR), together with Bu_3SnCH_2Cl.[14] The reaction was less stereoselective in DMF at –30 °C (*E*:*Z* 82:18). The best reaction conditions were found to be 2 equivalents of $Bu_3SnCHBr_2$ relative to the aldehyde and 1 equivalent of DMF (relative to $CrCl_2$) in THF, along with LiI (Eq. 3). Using 1.1 equivalents of $Bu_3SnCHBr_2$ relative to nonanal, for example, and keeping the rest of the conditions the same gave the stannane in only 28% yield. LiI presumably forms the extremely light sensitive Bu_3SnCHI_2[10] *in situ*, which is reduced to the active *gem*-dichromium species.

$$RCHO \xrightarrow[DMF,\ THF,\ 25\ ^\circ C]{Bu_3SnCHBr_2,\ LiI,\ CrCl_2} R \diagup\!\!=\!\!\diagdown SnBu_3 \qquad (3)$$

Reactions with unhindered aliphatic aldehydes gave exclusively the *E*-alkenylstannanes in reasonable yields (Table 1). However, pivalaldehyde was a poor substrate (6% yield of the *E*-alkenylstannane **9**). The successful separation of analytically pure non-polar stannanes (entries 1-3) from non-polar side-products (Bu_3SnMe and traces of Bu_3SnCH_2I[15]) was due to application of the reversed-phase chromatography technique recently reported by Farina.[16] With benzaldehyde, styrene was observed in the crude NMR

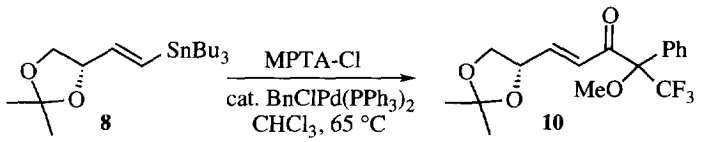
(alkenylstannane: styrene 74:26) and, in this case, the alkenylstannane co-chromatographed with Bu_3SnMe and Bu_3SnCH_2I (44:51:5 respectively (mole ratios), 50% yield of the alkenylstannane).

Table 1. Preparation of *E*-Alkenylstannanes from Aldehydes.

Entry	Aldehyde[17]	Alkenylstannane	Yield, %	Alkene[18]	Yield, %
1.	$C_8H_{17}CHO$	 **1**	60	—	
2.		 **2**	62	—	
3.		 **3**	60	—	
4.	$MeO_2C(CH_2)_4CHO$	$MeO_2C(CH_2)_4$  **4** (X = $SnBu_3$)	61	$MeO_2C(CH_2)_4$ 	34
5.	$NC(CH_2)_6CHO$	$NC(CH_2)_6$  **5**	58	$NC(CH_2)_6$ 	41
6.	$MeCO(CH_2)_{10}CHO$	$MeCO(CH_2)_{10}$  **6**	53	$MeCO(CH_2)_{10}$ 	36
7.		 **7**	58	—	
8.		 **8**	63	—	

It was important to examine the chemoselectivity of the process shown in Eq. 1 since, as noted earlier, this will be one of the major factors determining the utility of the reaction in synthesis. Ester, cyano and ketal groups are unaffected during alkenylstannane formation (Table 1, entries 4, 5 and 8). A keto-aldehyde gave mainly the homologated stannyl enone **6**, and a small amount (10%) of the alkenylstannane with the ketone also methylenated. Thus, although cyclododecanone was found to be partially methylenated under the reaction conditions in Eq. 3 to give methylenecyclododecane[19] (45%, 73% based on recovered ketone), a ketone is reasonably well tolerated in a competitive reaction with an aldehyde. 1,2-Attack on an α,β-unsaturated aldehyde (entry 7) indicates that the reaction provides a simple route to 1-tributylstannyl dienes, however in this case a mixture of geometrical isomers (83:17, *E*:*Z*) was obtained.

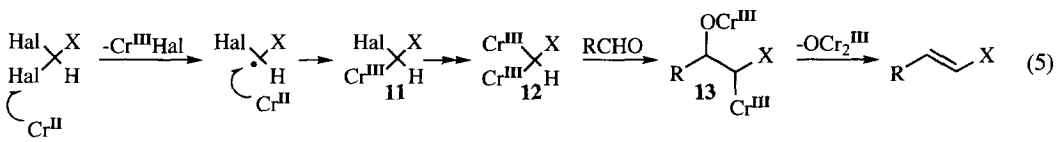
The susceptibility of an α-chiral aldehyde to epimerisation during the reaction was also examined. The e.e. of the stannane **8** derived from *R*-glyceraldehyde acetonide was determined to be ≥ 95% by Pd-catalysed cross-coupling with both racemic and *S*-Mosher's acid chlorides and inspection of the ^{1}H NMR alkenyl regions of the resulting enones **10** (Eq. 4). Whilst the cross-coupling yields were modest (35% and 49% respectively), racemic Mosher's acid chloride gave a 1:1 diastereomeric mixture of enones **10** which indicated that during the reactions there was no preference for the formation (or destruction) of a particular diastereomer.



8 10 (4)

High field ^{1}H NMR analyses of the crude materials from the reactions in Table 1 indicated that, apart from entry 7, the only alkenylstannane signals detectable in the alkenyl region were due to the *E*-isomers. However, in entries 4-6 the non-volatile alkenes resulting from methylenation of the aldehyde were also detected and easily separated chromatographically from the *E*-alkenylstannanes. We considered that the unwanted methylenated byproducts could have arisen from either limited stability of the alkenylstannanes under the reaction conditions, protodestannylation during work-up, or operation of a competitive methylenation reaction. Shortened reaction times (1-2 h instead of 24 h), or buffered work-up conditions, did not significantly alter the *E*-alkenylstannane:alkene ratio, whereas addition of I_2 just prior to work-up gave, in the case of entry 4, the iodoalkene **4** (X = I) (66%) exclusively as the *E*-isomer along with the simple methylenated material (27%). Therefore, it seems most likely that the alkene forms competitively alongside the *E*-alkenylstannane.

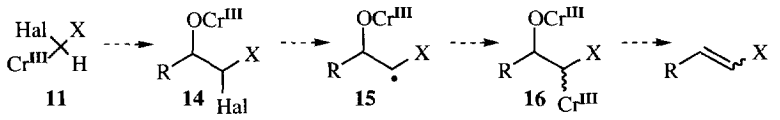
Mechanistically, the chromium(II)-mediated reactions of *gem*-dihalides with aldehydes are thought to proceed *via* two successive halogen atom transfers[20] to $CrCl_2$ where the intermediate radicals are immediately reduced to give ultimately a *gem*-dichromium species **12** which adds to the aldehyde to give **13** (Eq. 5). β-Elimination from **13** then occurs to provide predominantly or exclusively the *E*-alkene.



11 12 13 (5)

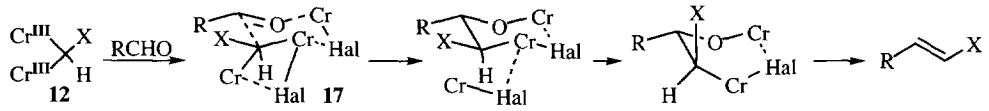
As alkylchromium reagents are known to add to aldehydes,[21] one may question that *gem*-dichromium reagents are valid intermediates and instead consider it possible that addition of the intermediate **11** to an aldehyde occurs to give the alkoxide **14** (Eq. 6). Halogen atom transfer from the alkoxide **14** to chromium(II) would then be followed by trapping of the intermediate radical **15** by another chromium(II) species to give **16**. However, deoxygenations of both *E*- and *Z*-2-butene epoxides with chromium complexes gave the same *E*:*Z* ratio of 2-butene (~55:45),[22] and treatment of 1,1-diiodo-2-tridecanol with $CrCl_2$ produced a 1:1 mixture of *E*- and *Z*-1-iodo-1-tridecenes.[11] As these reactions are likely to proceed through intermediates **15** and **16** (R =

X = Me for 2-butene preparation; R = $C_{11}H_{23}$, X = I for 1-iodo-1-tridecene preparation), it follows that *E*-alkene formation is not inherently favoured in the β-elimination step, but must be dependant on the relative *vic*-stereochemistry in **16**. That is, the carbon-chromium linkage in **16** is sufficiently stable to maintain stereochemical integrity until stereospecific β-elimination occurs. This β-elimination is likely to be a *syn* process.[22] The *E*:*Z* alkene ratio is then dependant on stereoselectivity in the addition of a particular *gem*-dichromium species to an aldehyde. A remaining question relates to the lack of reaction between the monoalkyl chromium intermediate **11** and an aldehyde. It seems that the stability of the halide-substituted monoalkylchromium **11** renders it a poor species to react with an aldehyde and activation as the *gem*-dichromium reagent **12** is required.



(6)

Given the importance of bridging halide ions in chromium chemistry,[23] a reasonable mechanism for the olefination reaction is shown in Eq. 7. The minor *Z*-alkene, or methylenated byproduct when X = $SnBu_3$, then arises from a less favourable transition state **17** (X and H interchanged) which, when X = $SnBu_3$, generally prefers to eliminate by a Peterson-type process[24] and generate an *E*-alkenyl chromium (which abstracts a H-atom from the solvent), rather than form the more hindered *Z*-alkene. The generally excellent stereoselectivity observed in chromium(II)-mediated synthesis of *E*-alkenylstannanes may then simply reflect loss by an alternative elimination pathway of the intermediate that would give rise to the *Z*-alkenylstannane.



(7)

In summary, the reactions of unhindered aliphatic aldehydes with a *gem*-dichromium reagent derived from $Bu_3SnCHBr_2$, LiI and $CrCl_2$ provide useful routes to *E*-alkenylstannanes. Application of the methodology in natural product synthesis is currently under investigation.[25]

EXPERIMENTAL

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under argon. Syringes and needles for the transfer of reagents were dried at 90 °C and allowed to cool in a desiccator over P_2O_5 before use. Ethers were distilled from sodium benzophenone ketyl; (chlorinated) hydrocarbons, Pr^i_2NH, Et_3N, and MeCN from CaH_2. DMF was distilled from CaH_2 under reduced pressure. Internal reaction temperatures are reported unless stated otherwise. All reactions were monitored by TLC using commercially available glass-backed plates, pre-coated with either a 0.25 mm layer of silica containing a fluorescent indicator (Merck), or a 0.2 mm layer of octadecylsilane bonded silica containing a fluorescent indicator (Whatman). Organic layers were evaporated with a Büchi rotary evaporator by using water-aspirator-reduced

pressure, followed by drying on a static oil pump (1 mm Hg). Column chromatography was carried out either on Kieselgel 60 (40-63 μm) using light petroleum (boiling range 40-60 °C) and Et_2O, or on Preparative C-18 (55-105 μm) (Millipore) using CH_2Cl_2 and MeCN. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Microanalyses were performed by MEDAC at Brunel University. IR spectra were recorded as thin films unless stated otherwise, using a Perkin-Elmer 881 spectrophotometer with polystyrene film for calibration (1602 and 1029 cm^{-1}). Peak intensities are specified as strong (s), medium (m) or weak (w). ^1H NMR spectra were recorded in $CDCl_3$ with Bruker WM250 or JEOL EX400 spectrometers operating at 250.14 MHz and 399.65 MHz respectively. Chemical shifts are reported relative to $SiMe_4$ or, where stated, to residual $CHCl_3$ (δ 7.25) in sample. Coupling constants (*J*) are given in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ on the Bruker at 62.90 MHz or on the JEOL at 100.40 MHz. Chemical shifts are reported relative to $CDCl_3$ (central line of triplet, δ 77.0). A mixture of off-resonance, DEPT 135, and DEPT 90 pulse sequences were used to aid spectral interpretation. Mass spectra were obtained from the EPSRC Mass Spectrometry Service Centre, Swansea with a VG Micromass ZAB-E instrument.

Dibromomethyl(tributyl)stannane. Bu^nLi (40 ml, 1.50 M in hexanes, 0.06 mol) was added from a dropping funnel to a mechanically stirred solution of Pr^i_2NH (10 ml, 0.071 mol) in THF (70 ml) and Et_2O (100 ml) at 0 °C under argon. After 15 min at 0 °C the reaction mixture was cooled to –95 °C ($MeOH/N_2$-bath) and a solution of CH_2Br_2 (7.3 ml, 0.065 mol) in THF (50 ml) was added from the dropping funnel such that the reaction temperature remained between –95 °C and –90 °C. After 15 min at –90 °C a solution of Bu_3SnCl (16.317 g, 0.050 mol) in THF (50 ml) was added from the dropping funnel such that the reaction temperature remained between –95 °C and –90 °C. On completion of the addition, the reaction was allowed to warm to –63 °C and then quenched by the addition of saturated aqueous NH_4Cl solution (8 ml). The cooling bath was removed and the mixture allowed to warm rapidly to room temperature before removal of most of the solvents by rotary evaporation under reduced pressure. The concentrate was diluted with water (150 ml) and light petroleum (250 ml), and then filtered through Celite 545 (Fluka) to remove small amounts of a fine white precipitate. The organic layer was separated and the aqueous layer extracted with additional light petroleum (250 + 100 ml). The combined organic layers were dried ($MgSO_4$) and concentrated by rotary evaporation under reduced pressure, followed by standing on a static oil pump to constant weight. The crude material (22.852 g) was essentially pure by TLC and ^1H NMR. Purification by column chromatography (700 g SiO_2, light petroleum, 150 ml fractions) gave a colourless oil on concentration of fractions 10-16, *dibromomethyl(tributyl)stannane* (20.585 g, 89%); R_f 0.5 (light petroleum) (Found: C, 33.45; H, 6.0. $C_{13}H_{28}Br_2Sn$ requires C, 33.7; H, 6.1%); ν_{max}/cm^{-1} 2954s, 2920s, 2868s, 2849s, 1463m, 1377m, 1075m, 876m, 693m and 665m; δ_H(250 MHz; $CHCl_3$) 5.31 (1 H, s, J_{Sn-H} 10, $CHBr_2$), 1.66-1.51 (6 H, m, $(CH_2CH_2)_3Sn$) 1.34 (6 H, sxt, *J* 7, 3 x $MeCH_2$), 1.16-1.09 (6 H, m, $(CH_2)_3Sn$) and 0.91 (9 H, t, *J* 7, 3 x Me); δ_C(63 MHz) 28.5 (J_{Sn-C} 20, $(CH_2CH_2)_3Sn$), 28.3 (J_{Sn-C} 153, $CHBr_2$), 27.3 (J_{Sn-C} 58 , 3 x $MeCH_2$), 13.6 (3 x Me) and 11.7 ($J_{119Sn-C}$ 341, $J_{117Sn-C}$ 335 , $(CH_2)_3Sn$); *m/z* (EI) 349 (5%), 313 (10), 291 (30), 257 (5), 235 (20), 199 (20), 179 (30), 121 (10) and 57 (100). Further elution gave a colourless oil, bis(*dibromomethyl*)-*dibutylstannane* (0.944 g, 3%); R_f 0.36 (light petroleum); ν_{max}/cm^{-1} 2957s, 2922s, 2871s, 2854s, 1464m, 1133m, 698m and 663m; δ_H(250 MHz; $CHCl_3$) 5.39 (2 H, s, J_{Sn-H} 8, $(CHBr_2)_2$), 1.81-1.68 (4 H, m, $(CH_2CH_2)_2Sn$), 1.54-1.46 (4 H, m, $(CH_2)_2Sn$), 1.41 (4 H, sxt, *J* 7, 2 x $MeCH_2$), and 0.94 (6 H, t, *J* 7, 2 x Me);

δ_C (63 MHz) 28.0 (J_{Sn-C} 24, (CH_2CH_2)$_2$Sn), 27.5 (J_{Sn-C} 220, ($CHBr_2$)$_2$), 27.2 (J_{Sn-C} 67, 2 x MeCH_2), 13.6 (2 x Me) and 13.2 ($J_{119Sn-C}$ 382, $J_{117Sn-C}$ 365, (CH_2)$_2$Sn); *m/z* (EI) 386 (5%), 372 (3), 348 (15), 295 (5), 198 (20), 173 (5) 120 (5) and 57 (100).

Typical procedure for the preparation of E-*alkenylstannanes*

(E)-Tributyl(1-decenyl)stannane **1**. Dry, deoxygenated DMF (0.78 ml, 10 mmol) was added dropwise to a well-stirred slurry of $CrCl_2$ (Aldrich, 95% w/w pure; 1.33 g, 10 mmol) in dry, deoxygenated THF (16 ml) under argon at 25 °C. After 15 min a mixture of nonanal (144 mg, 1 mmol) and dibromomethyl-(tributyl)stannane (926 mg, 2 mmol) in dry, deoxygenated THF (4 ml) was added dropwise to the reaction mixture. The flask was covered with aluminium foil to exclude light and then anhydrous LiI (1 M in dry, deoxygenated THF; 4 ml, 4 mmol) was added dropwise. After 40 h at 25 °C water (30 ml) was added and the mixture was extracted with light petroleum (3 x 20 ml). The combined organic layers were washed successively with water (20 ml) and brine (20 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the residue by reversed-phase flash chromatography (C-18, 30% CH_2Cl_2/MeCN) gave a colourless oil, *stannane* **1** (260 mg, 60%);[4a] R_f 0.18 (20% CH_2Cl_2/MeCN) [Found: (M-Bu)$^+$, 373.1917. $C_{18}H_{37}Sn$ requires *m/z*, 373.19173]; υ_{max}/cm^{-1} 2987s, 2959s, 2931m, 2874m, 2869m, 1746m, 1503m, 1387m, 1355m, 1216s and 1068s; δ_H(250 MHz; $CHCl_3$) 5.95 (1 H, dt, *J* 19 and 5, $J_{119Sn-H}$ 68, $J_{117Sn-H}$ 65, C*H*=CHSn), 5.83 (1 H, d, *J* 19, $J_{119Sn-H}$ 79, $J_{117Sn-H}$ 76, =CHSn), 2.17-2.07 (2 H, m, CH_2CH=), 1.65-1.17 (24 H, m, Sn($CH_2CH_2CH_2$)$_3$ and 6 x CH_2), 0.99-0.71 [18 H, m, Sn(C$H_2CH_2CH_2Me$)$_3$, incl. at 0.88 (3 H, t, *J* 7, 3 x Me)]; δ_C(63 MHz) 149.8 (HC=), 126.9 ($J_{119Sn-C}$ 397, $J_{117Sn-C}$ 384, =CSn), 38.0 (J_{Sn-C} 63, CH_2CH=), 32.1 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (4 x CH_2), 29.1 (CH_2), 27.4 (J_{Sn-C} 52, 3 x CH_2Me), 22.8 (CH_2), 14.2 (Me), 13.7 (3 x Me) and 9.5 ($J_{119Sn-C}$ 340, $J_{117Sn-C}$ 325, Sn(CH_2)$_3$); *m/z* (EI) 373(100%), 329(20), 317(60), 291(20), 261(70) and 177(30).

Analytical data for E-*alkenylstannanes*

(E)-Tributyl[2-(cyclohexyl)ethenyl]stannane **2**. A colourless oil (237 mg, 62%) was obtained from cyclohexanecarboxaldehyde (108 mg, 0.96 mmol) after reversed-phase flash chromatography (C-18, gradient elution, 20% to 30% CH_2Cl_2/MeCN); R_f 0.29 (20% CH_2Cl_2/MeCN) [Found: (M-Bu)$^+$, 343.1448. $C_{16}H_{31}{}^{120}Sn$ requires *m/z*, 343.14477]; ν_{max}/cm^{-1} 2958s, 2924s, 2872s, 1597m, 1465m, 1450m, 1377m, 989m, 691m and 663m; δ_H(250 MHz; $CHCl_3$) 5.90 (1 H, dd, *J* 19 and 5, $J_{119Sn-H}$ 70, $J_{117Sn-H}$ 67, C*H*=CHSn), 5.79 (1 H, d, *J* 19, $J_{119Sn-H}$ 79, $J_{117Sn-H}$ 76, =CHSn), 2.05-1.89 (1 H, m, C*H*CH=), 1.78-0.98 (22 H, m, Sn($CH_2CH_2CH_2$)$_3$ and 5 x CH_2) and 0.98-0.71 [15 H, m, Sn(C$H_2CH_2CH_2Me$)$_3$, incl. at 0.88 (9 H, t, *J* 7, 3 x Me)]; δ_C(63 MHz) 155.4 (HC=), 123.5 ($J_{119Sn-C}$ 404, $J_{117Sn-C}$ 385, =CSn), 45.2 (J_{Sn-C} 59, CH_2CH=), 32.7 (2 x CH_2), 29.2 (J_{Sn-C} 20, Sn(CH_2CH_2)$_3$), 27.3 (J_{Sn-C} 52, 3 x CH_2Me), 26.4 (CH_2), 26.2 (2 x CH_2), 13.7 (3 x Me) and 9.5 ($J_{119Sn-C}$ 339, $J_{117Sn-C}$ 324 Sn(CH_2)$_3$); *m/z* (EI) 395 (10%), 343 (100), 287 (35), 231 (30) and 177 (10).

(E)-Tributyl(1-hepten-6-ynyl)stannane **3**. A colourless oil (232 mg, 60%) was obtained from 5-hexynal (97 mg, 1 mmol) after reversed-phase flash chromatography (C-18, 5% CH_2Cl_2/MeCN); R_f 0.34 (5% CH_2Cl_2/MeCN) [Found: (M-Bu)$^+$, 327.1135. $C_{15}H_{27}{}^{120}Sn$ requires *m/z*, 343.11347]; ν_{max}/cm^{-1} 3313m,

2956s, 2927s, 2871s, 2853s, 2120w, 1599m, 1464m, 1377m, 1072m, and 631s; δ_H(250 MHz; $CHCl_3$) 6.09-5.78 (2 H, m, CH=CHSn), 2.30-2.17 [4 H, m, $\equiv CCH_2$ and CH_2CH=, incl. at 2.21 (2 H, td, *J* 7 and 2.5, $\equiv CCH_2$)], 1.97 (1 H, t, *J* 2.5, HC≡C), 1.66 (2H, qui, *J* 7, CH_2), 1.57-1.25 (12 H, m, $Sn(CH_2CH_2CH_2)_3$) and 0.98-0.84 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.91 (9 H, t, *J* 7, 3 x Me)]; δ_C(63 MHz) 148.0 (HC=), 128.5 ($J_{119Sn-C}$ 394, $J_{117Sn-C}$ 376, =CSn), 84.2 (HC≡*C*), 68.2 (*H*C≡C), 36.7 (J_{Sn-C} 63, CH_2CH=), 29.1 (J_{Sn-C} 20, $Sn(CH_2CH_2)_3$), 27.7 ($HC{\equiv}CCH_2CH_2$), 27.2 (J_{Sn-C} 52, 3 x CH_2Me), 17.7 ($HC{\equiv}CCH_2$), 13.6 (3 x Me) and 9.4 ($J_{119Sn-C}$ 341, $J_{117Sn-C}$ 326, $Sn(CH_2)_3$); *m/z* (EI) 327 (80%), 291 (20), 269 (100), 213 (90), 177 (40) and 121 (40).

Methyl (E)-7-tributylstannyl-6-heptenoate **4** (X = $SnBu_3$). A colourless oil (266 mg, 61%) was obtained from methyl 6-oxohexanoate (144 mg, 1 mmol) after flash chromatography (SiO_2, 5% Et_2O/light petroleum with a few drops of Et_3N added); R_f 0.28 (5% Et_2O/light petroleum) [Found: $(M+H)^+$, 433.2110. $C_{20}H_{41}O_2{}^{120}Sn$ requires *m/z*, 433.21286]; υ_{max}/cm^{-1} 2955s, 2926s, 2871s, 2853s, 1743s, 1599m, 1464m, 1435m, 1197m, 1172m and 990m; δ_H(400 MHz) 5.94 (1 H, dt, *J* 19 and 5, *CH*=CHSn), 5.87 (1 H, d, *J* 19, =CHSn), 3.66 (3 H, s, MeO), 2.32 (2 H, t, *J* 7, $COCH_2$), 2.14 (2 H, dt, *J* 8 and 5, CH_2CH=) and 1.70-1.05 (16 H, m, $Sn(CH_2CH_2CH_2)_3$ and $(CH_2)_2CH_2CH$=) and 1.03-0.82 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.89 (9 H, t, *J* 8, 3 x Me)]; δ_C(100 MHz) 173.9 (C=O), 148.8 (HC=), 127.7 ($J_{119Sn-C}$ 396, $J_{117Sn-C}$ 380, =CSn), 51.3 (MeO), 37.4 (J_{Sn-C} 32, CH_2CH=), 33.9 ($COCH_2$), 29.4 (J_{Sn-C} 20, $Sn(CH_2CH_2)_3$), 28.4 (CH_2), 27.2 (J_{Sn-C} 59, 3 x CH_2Me), 24.4 (CH_2), 13.6 (3 x Me) and 9.4 ($J_{119Sn-C}$ 341, $J_{117Sn-C}$ 327, $Sn(CH_2)_3$); *m/z* (EI) 375 (100%), 319 (20), 201 (20), 149 (25), 135 (15) and 121 (20).

(E)-9-Tributylstannyl-8-nonenenitrile **5**. A colourless oil (248 mg, 58%) was obtained from 8-oxo-octanenitrile (139 mg, 1 mmol) after flash chromatography (SiO_2, 10% Et_2O/light petroleum with a few drops of Et_3N added); R_f 0.31 (10% Et_2O/light petroleum) [Found: $(M-Bu)^+$ 370.1557. $C_{17}H_{32}N^{120}Sn$ requires *m/z*, 370.15566]; υ_{max}/cm^{-1} 2959s, 2926s, 2870s, 2854s, 2246w, 1727m, 1590m, 1464m, 1263s, 1072s and 1021m; δ_H(400 MHz) 5.94 (1 H, dt, *J* 19 and 6, *CH*=CHSn), 5.86 (1 H, d, *J* 19, =CHSn), 2.33 (2 H, t, *J* 7, $NCCH_2$), 2.13 (2 H, m, CH_2CH=), 1.66 (2 H, qui, *J* 7, $NCCH_2CH_2$), 1.55-1.26 (18 H, m, $Sn(CH_2CH_2CH_2)_3$ and $(CH_2)_3CH_2CH$=) and 0.98-0.75 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.88 (9 H, t, *J* 7, $Sn(CH_2CH_2CH_2Me)_3$]; δ_C(100 MHz) 149.2 (HC=), 127.5 (J_{Sn-C} 77, =CSn), 119.8 (NC), 37.6 (J_{Sn-C} 62, CH_2CH=), 29.1 (J_{Sn-C} 20, $Sn(CH_2CH_2)_3$), 28.5 (2 x CH_2), 28.2 (CH_2), 27.3 (J_{Sn-C} 54, 3 x CH_2Me), 25.4 (CH_2), 17.1 (CH_2), 13.8 (3 x Me) and 9.4 ($J_{119Sn-C}$ 335, $J_{117Sn-C}$ 325, $Sn(CH_2)_3$); *m/z* (EI) 370 (100%), 314 (30), 256 (15), 177 (10), 148 (10) and 121 (15).

(E)-14-Tributylstannyl-13-tetradecen-2-one **6**. A colourless oil (265 mg, 53%) was obtained from 12-oxotridecanal (212 mg, 1 mmol) after flash chromatography (SiO_2, 8% Et_2O/light petroleum with a few drops of Et_3N added); R_f 0.31 (10% Et_2O/light petroleum) [Found: $(M+H)^+$ 501.3120. $C_{26}H_{53}O^{120}Sn$ requires *m/z*, 501.31200]; υ_{max}/cm^{-1} 2959s, 2926s, 2870s, 2854s, 2246w, 1727m, 1590m, 1464m, 1263s, 1072s and 1021m; δ_H(400 MHz) 5.94 (1 H, dt, *J* 19 and 6, *CH*=CHSn), 5.85 (1 H, d, *J* 19, =CHSn), 2.41 (2 H, t, *J* 7, $MeCOCH_2$), 2.13 (3 H, s, MeCO), 2.11 (2 H, q, *J* 7, CH_2CH=), 1.58-1.23 (28 H, m, $Sn(CH_2CH_2CH_2)_3$ and $(CH_2)_8CH_2CH$=) and 0.94-0.82 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.89 (9 H, t, *J* 7, 3 x Me)]; δ_C(100

MHz) 209.4 (CO), 149.9 (HC=), 126.9 (J_{Sn-C} 77, =CSn), 44.1 ($COCH_2$), 38.2 (J_{Sn-C} 62, CH_2CH=), 30.1 (*Me*CO), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 ($Sn(CH_2CH_2)_3$), 29.2 (CH_2), 27.6 (J_{Sn-C} 53, 3 x CH_2Me), 24.2 (CH_2), 14.0 (3 x Me) and 9.7 ($J_{119Sn-C}$ 341, $J_{117Sn-C}$ 325, $Sn(CH_2)_3$); *m/z* (EI) 443 (100%), 387 (10), 205 (40), 177 (30), 149 (20) and 121 (20).

(E)- and (Z)-Tributyl(4-methyl-1,3-pentadienyl)stannane **7**. A colourless oil [203 mg, 58% (*E*:*Z*, 83:17 determined by integration of peaks at 6.03 and 5.89 on ^{1}H nmr)] was obtained from 3-methyl-2-butenal (91 mg, 1 mmol) after reversed-phase flash chromatography (C-18, 10% CH_2Cl_2/MeCN); R_f 0.30 (10% CH_2Cl_2/MeCN) [Found: (M-Bu)$^+$, 315.1135. $C_{14}H_{27}{}^{120}Sn$ requires *m/z*, 315.11348]; υ_{max}/cm^{-1} 2957s, 2923s, 2871s, 2853s, 1645m, 1566w, 1466m, 1378m, 1343 and 993m; *m/z* (EI) 315 (25%), 249 (55), 193 (100), 177 (20), 135 (80) and 121 (40); data for *(E)-tributyl(4-methyl-1,3-pentadienyl)stannane*: δ_H(250 MHz; CD_2Cl_2) 6.72 (1 H, dd, *J* 19 and 10, $J_{119Sn-H}$ 63, $J_{117Sn-H}$ 59, C*H*=CHSn), 6.03 (1 H, d, *J* 19, =CHSn), 5.84-5.77 (1 H, br d, *J* 10, =CH), 1.77 (3 H, q, *J* 1, Me), 1.75 (3 H, q, *J* 1, Me), 1.60-1.20 (12 H, m, $Sn(CH_2CH_2CH_2)_3$), 0.95-0.75 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.87 (9 H, t, *J* 7, 3 x Me)]; δ_C(100 MHz) 143.3 (HC=), 134.4 ($(Me)_2C$=), 130.2 (C=CH), 128.7 (J_{Sn-C} 73.6, =CSn), 29.1 (J_{Sn-C} 20, $Sn(CH_2CH_2)_3$), 28.4 (Me), 27.2 (J_{Sn-C} 59, 3 x CH_2Me), 24.4 (Me), 13.6 (3 x Me) and 9.4 ($J_{119Sn-C}$ 341, $J_{117Sn-C}$ 327, $Sn(CH_2)_3$); discernible data for *(Z)-tributyl(4-methyl-1,3-pentadienyl)stannane*: δ_H(250 MHz; CD_2Cl_2) 7.24 (1 H, dd, *J* 13 and 11, C*H*=CHSn), 5.89 (1 H, d, *J* 13, =CHSn), 5.76-5.70 (1 H, br d, *J* 11, =CH), 1.77 (3 H, q, *J* 0.5, Me), 1.75 (3 H, q, *J* 0.5, Me); δ_C(100 MHz) 142.6 (HC=), 136.4 ($(Me)_2C$), 132.0 (C=CH), 128.2 (=CSn), 29.1 ($Sn(CH_2CH_2)_3$), 25.9 (Me), 27.3 ($J_{119Sn-C}$ 55, $J_{117Sn-C}$ 44, 3 x CH_2Me), 18.4 (Me), 13.7 (3 x Me) and 9.5 ($J_{119Sn-C}$ 342, $J_{117Sn-C}$ 327, $Sn(CH_2)_3$).

[S-(E)]-4-[2-(Tributylstannyl)ethenyl]-2,2-dimethyl-1,3-dioxolane **8**. A colourless oil (258 mg mg, 63%) was obtained from *R*-glyceraldehyde acetonide (130 mg, 1 mmol) after flash chromatography (SiO_2, 3% Et_2O/light petroleum with a few drops of Et_3N added). R_f 0.30 (3% Et_2O/light petroleum); $[\alpha]_D^{20}$ +39.0 (*c* 1.25 in benzene) [Found: (M-Bu)$^+$, 361.1189. $C_{15}H_{29}O^{120}Sn$ requires *m/z*, 361.11896]; ν_{max}/cm^{-1} 2958s, 2927s, 2871s, 2854s, 1602w, 1464m, 1457m, 1378m, 1369m, 1260s and 1062s; δ_H(400 MHz) 6.23 (1 H, dd, *J* 19 and 1, $J_{119Sn-H}$ 66, $J_{117Sn-H}$ 63, =CHSn), 5.89 (1 H, dd, *J* 19 and 7, $J_{119Sn-H}$ 60, $J_{117Sn-H}$ 57, C*H*=CHSn), 4.40 (1 H, m, C*H*CH=), 4.03 (1 H, dd, *J* 8 and 6, H of OCH_2), 3.53 (1 H, t, *J* 8, H of OCH_2), 1.49-1.10 [18 H, m, $Sn(CH_2CH_2CH_2)_3$) and CMe_2, incl. at 1.37 (3 H, s, Me) and 1.32 (3 H, s, Me)], 0.91-0.76 [15 H, m, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.88 (9 H, t, *J* 7, 3 x Me)]; δ_C(100 MHz) 145.2 (HC=), 133.2 ($J_{119Sn-C}$ 360, $J_{117Sn-C}$ 343, =CSn), 109.2 (Me_2C), 80.0 (J_{Sn-C} 66, CHCH=), 69.3 (OCH_2), 29.0 (J_{Sn-C} 20, $Sn(CH_2CH_2)_3$), 27.2 (J_{Sn-C} 55, 3 x CH_2Me), 26.7 (Me), 25.9 (Me), 13.7 (3 x Me) and 9.4 ($J_{119Sn-C}$ 348, $J_{117Sn-C}$ 331, $Sn(CH_2)_3$); *m/z* (EI) 361 (75%), 308 (50), 291 (100) and 247 (20).

(E)-Tributyl(3,3-dimethyl-1-butenyl)stannane **9**. A colourless oil (23 mg, 6%) was obtained from pivalaldehyde (88 mg, 1 mmol) after reversed-phase flash chromatography (C-18, 10% CH_2Cl_2/MeCN); R_f 0.27 (10% CH_2Cl_2/MeCN) [Found: (M-Bu)$^+$, 317.1290. $C_{14}H_{29}{}^{120}Sn$ requires *m/z*, 317.12912]; ν_{max}/cm^{-1} 2956s, 2925s, 2871s, 2855s, 1593m, 1475m, 1463s, 1376m, 1361m, 1260m and 993s; δ_H(250 MHz; $CHCl_3$) 5.95 (1 H, d, *J* 19, $J_{119Sn-H}$ 70, $J_{117Sn-H}$ 68, C*H*=CHSn), 5.75 (1 H, d, *J* 19, $J_{119Sn-H}$ 79, $J_{117Sn-H}$ 75, =CHSn),

1.55-1.41 (6 H, m, 3 x CH_2), 0.99 (9 H, s, Bu^t) and 0.91-0.82 [15 H, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.86 (9 H, t, *J* 7, 3 x Me)]; δ_C(63 MHz) 160.0 (HC=), 119.7 (=CSn), 35.9 (Me_3C), 29.2 (Me_3C), 29.1 (J_{Sn-C} 21, $Sn(CH_2CH_2)_3$), 27.2 (J_{Sn-C} 52, 3 x CH_2Me), 13.7 (3 x Me) and 9.5 ($J_{119Sn-C}$ 340, $J_{117Sn-C}$ 325 $Sn(CH_2)_3$); *m/z* (EI) 317 (100%), 261 (60), 205 (60), 117 (20), 135 (25) and 121 (30).

[2R,5(4S)-(E)]-1,1,1-Trifluoro-2-methoxy-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-phenyl-4-penten-3-one **10**. A solution of stannane **8** (167 mg, 0.4 mmol) in $CHCl_3$ (1 ml) was added to a small Carius tube containing a stirred solution of (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (164 mg, 0.48 mmol) and benzyl(chloro)bis(triphenylphosphine)palladium(II) (10 mg, 0.01 mmol) in $CHCl_3$ (2 ml). The tube was sealed and heated to 65 °C for 24 h. The tube was then opened and the reaction mixture filtered and evaporated under reduced pressure. Purification of the residue twice by flash column chromatography (SiO_2, first with 50% Et_2O/petroleum ether as the eluant and then secondly with 20% Et_2O/light petroleum as the eluant; DBN[26] (5 drops) was added to the crude oil in 0.5 ml of the eluant prior to loading the second column) gave a colourless oil, *enone* **10** (67 mg, 49%). R_f 0.23 (20% Et_2O/light petroleum); $[\alpha]_D^{20}$ +74.8 (*c* 5 in $CHCl_3$) [Found: (M+H)+, 345.1314. $C_{17}H_{20}O_4F_3$ requires *m/z*, 345.13148]; υ_{max}/cm^{-1} 2987s, 2938s, 2877m, 2849m, 1710s, 1453s, 1383m, 1374s, 1270s, 1168s and 1064s; δ_H(250 MHz) 7.49-7.29 (5 H, m, Ar), 7.02 (1 H, dd, *J* 16 and 5, C*H*=CHCO), 6.52 (1 H, dd, *J* 16 and 1, =CHCO), 4.60 (1 H, m, CH_2CH), 4.12 (1 H, dd, *J* 8 and 7, C*H*HCH), 3.62 (1 H, dd, *J* 8 and 7, CH*H*CH), 3.59 (3 H, q, J_{H-F} 2, OMe), 1.39 (3 H, s, Me) and 1.34 (3 H, s, Me); δ_C(100 MHz) 192.2 (CO), 146.3 (=*C*HCO), 131.9 (COC*C*(Ar)), 129.6 (*C*H(Ar)), 128.5 (*C*H(Ar)), 127.3 (*C*H(Ar)), 124.3 (*C*H=CHCO), 123.5 (Q, J_{C-F} 2.9, CF_3), 110.4 ($(Me)_2C$), 86.1 (q, *J* 0.3, *C*CF_3), 75.1 (CH_2CH), 68.4 (CH_2), 55.9 (OMe), 26.5 (Me) and 25.7 (Me); δ_F(235.3 MHz; $CHCl_3$; CF_3CH_2OH) 2.92; *m/z* (EI) 345 (20%), 329 (20), 313 (30), 269 (40), 189 (70) and 155 (100).

[2R,5(4S)-(E)]- and *[2S,5(4S)-(E)]-1,1,1-Trifluoro-2-methoxy-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-phenyl-4-penten-3-one* **10**. Following the procedure for the 2*S* 5(4*S*) enone **10**, stannane **8** (70 mg, 0.17 mmol) was cross-coupled with (±)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (51 mg, 0.20 mmol). Purification was carried out by flash column chromatography (SiO_2, 20% Et_2O/light petroleum as the eluant, DBN[26] (5 drops) being added to the crude oil in 0.5 ml of the eluant prior to loading the column. This gave a colourless oil, *2R,5(4S)-* and *2S,5(4S)-enone* **10** (20 mg, 35%). R_f 0.23 (20% Et_2O/light petroleum) [Found: (M+H)+, 345.1314. $C_{17}H_{20}O_4F_3$ requires *m/z*, 345.13148]; υ_{max}/cm^{-1} 2987s, 2938s, 2877m, 2849m, 1710s, 1453s, 1383m, 1374s, 1270s, 1168s and 1064s; *m/z* (EI) 345(20%), 329(20), 313(30), 269(40), 189(70) and 155(100); discernible data for *2S,5(4S)*-enone **10**; δ_H(250 MHz) 7.01 (1 H, dd, *J* 16 and 5, C*H*CHCO), 6.48 (1 H, dd, *J* 15 and 2, CHCO), 4.13 (1 H, dd, *J* 9 and 7, C*H*HCH), 3.60 (1 H, dd, *J* 8 and 7, CH*H*CH), 3.58 (3 H, q, J_{H-F} 2, OCH_3), 1.42 (3 H, s, CH_3) and 1.36 (3 H, s, CH_3); δ_C(100 MHz) 129.5 (*C*(Ar)CCO), 124.4 (*C*HCHCO), 75.0 (CH_2CH), 68.5 (CH_2) and 25.7 (CH_3); δ_F(235.3 MHz, $CHCl_3$; CF_3CH_2OH) 2.77.

Methyl (E)-7-iodo-6-heptenoate **4** (X = I). Dry, deoxygenated DMF (0.78 cm^3, 10 mmol) was added dropwise to a well-stirred slurry of $CrCl_2$ (Aldrich, 95% w/w pure; 1.33 g, 10 mmol) in dry, deoxygenated THF (16 ml) under argon at 25 °C. After 15 min a mixture of methyl 6-oxohexanoate (0.144 g, 1 mmol) and dibromomethyl(tributyl)stannane (926 mg, 2 mmol) in dry, deoxygenated THF (4 ml) was added dropwise to

the reaction mixture. The flask was covered with aluminium foil to exclude light and then anhydrous LiI (1 M in dry, deoxygenated THF; 4 ml, 4 mmol) was added dropwise. After 24 h at 25 °C iodine (1.0 g, 3.9 mmol) was added to the reaction. After a further 5 min light petroleum (10 ml) was added followed by water (10 ml). The organic layer was washed with brine (2 x 10 ml), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by flash column chromatography (40 g SiO_2, 8% Et_2O/light petroleum) gave a colourless oil, *iodide* **4** (X = I) (0.177 g, 66%). R_f 0.27 (8% Et_2O/ light petroleum) [Found: $(M+NH_4)^+$, 286.0304. $C_8H_{17}INO_2$ requires *m/z*, 286.03041]; υ_{max}(neat)/cm^{-1} 3447s, 3054m, 2928s, 2857s, 2337m, 1737s, 1638m, 1606m, 1435m, 1197s, 1172s and 949m; δ_H(400 MHz) 6.48 (1H, dt, *J* 14 and 7, CH=), 5.99 (1H, dt, *J* 14 and 1, =CHI), 3.67 (3H, s, MeO), 2.30 (2H, t, *J* 7, $COCH_2$), 2.07 (2H, dtd, *J* 7, 7 and 1, CH_2CH=), 1.68 - 1.57 (2H, m, CH_2) and 1.50-1.36 (2H, m, CH_2); δ_C(75 MHz) 173.7 (C=O), 145.8 (CH_3O), 74.9 (=CHI), 51.4 (CH=), 35.5 ($COCH_2$), 33.6 (CH_2CH=), 27.7 (CH_2) and 24.1 (CH_2); *m/z* (EI) 286 (100%), 269 (10), 237 (10), 173 (25), 160 (40) and 141 (90).

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