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Synthesis of α-stannyl α,β-unsaturated carboxylic esters

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Abstract

A synthetic method for the preparation of α-stannyl α,β-unsaturated esters is described. The lithium enolate derived from tert-butyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)acetate reacts with aldehydes to give moderate to good yields of α-stannylated products. The method is not applicable to enolizable ketones.

1. Introduction

Functionalized organotin compounds have numerous applications in synthetic chemistry [1]. In this context, vinylstannanes have been especially important. Readily available by hydrostannation of alkynes, vinyltin compounds participate in a variety of synthetically useful transformations such as transmetallations [2], electrophilic destannylations [3] and palladium-catalyzed coupling reactions [4].

α-Stannyl α,β-unsaturated esters are a particularly interesting class of functionalized vinylstannanes. The combination of the vinylic organometallic substituent with the α,β-unsaturated carboxylic functionality offers tremendous possibilities for applications in organic synthesis. We have shown that these compounds undergo transmetallation reactions [5] and palladium-catalyzed coupling reactions with organic halides [6].

Addition of trialkyltin hydride to α,β-acetylenic esters has been reported to give mixtures of α- and β-stannyl α,β-unsaturated esters whose separation is difficult [7–9]. In some cases, the β-isomer can be obtained as the major product by appropriate choice of the alcoholic moiety of the starting alkynoate [10]. β-Stannyl esters are also available *via* 1,4-addition of trialkylstannylmetal reagents to suitable substrates [11,12]. However, to our knowledge no procedure of preparative value for the synthesis of the α-stannyl isomers has been described in the literature. Consequently, as part of our studies on the design and synthetic applications of new organotin reagents, we became interested in developing a practical method for the preparation of α-stannyl α,β-unsaturated esters.

The synthesis of α,β-unsaturated carboxylic esters from the reaction of α-silylated ester enolates with carbonyl compounds has emerged as an important synthetic tool in organic chemistry [13–15]. This variant of the original dehydroxysilylation reaction reported by Peterson [16] is thought to proceed *via* formation of β-oxidosilane (**3**), which undergoes a 1,3-migration of silicon from carbon to oxygen to generate β-silyloxy enolate (**4**), followed by β-elimination (Scheme 1) [15,17,18]. Syntheses of α-chloro [19] and α-trimethylsilyl [20] α,β-unsaturated esters were reported using this procedure. Thus, given the apparent versatility of this olefination process, we decided to examine its utility in the synthesis of α-stannyl α,β-unsaturated esters. In this paper we present a full account of our investigations in this area [21].

2. Results and discussion

Our synthetic route towards α-stannyl α,β-unsaturated esters is shown in Scheme 2. The required α-(tri-*n*-butylstannyl)-α-(trimethylsilyl)acetates (**8–9**) were conveniently prepared by our previously published stannylation procedure [22]. As a crude product, tert-butyl ester **8** was obtained in high yield (95–98%) and > 90% pure, as estimated by ^{1}H NMR. Extensive decomposition occurred during vacuum distillation or chromatography on silica gel lowering the yield of

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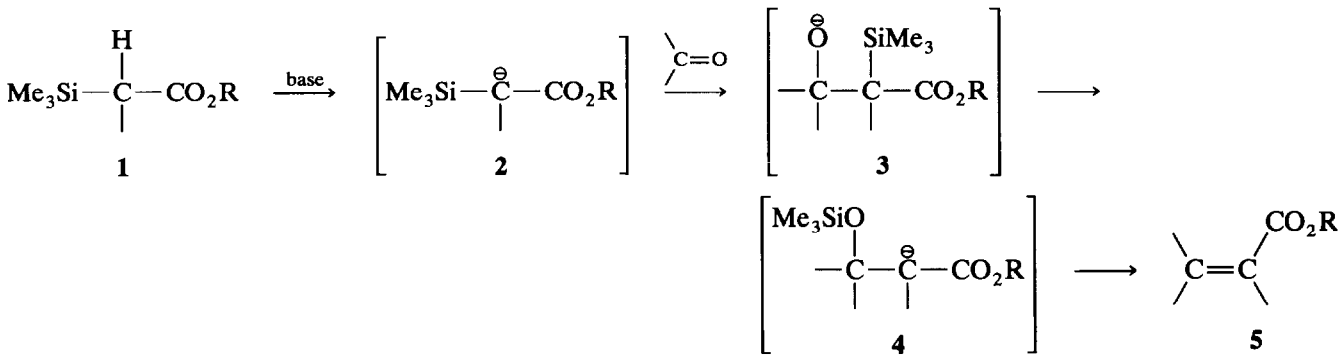


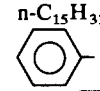
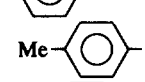
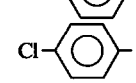
Scheme 1.

purified product to 60–75%. Therefore, crude ester **8** was used in the next step without purification. Ethyl ester **9** proved to be even less stable than its tert-butyl analogue and decomposed faster on standing and during purification. In the best case, compound **9** was obtained in 23% yield after chromatography on silica gel.

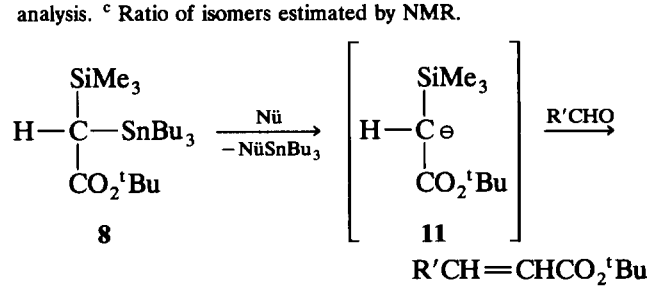
Enolate formation was examined using tert-butyl ester **8**. In our preliminary communication of this work [21], we reported that treatment of **8** with 1.1 equivalents of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) containing two equivalents of hexamethylphosphoramide (HMPA) at −23°C for 30 min, followed by addition of the corresponding aldehyde afforded the desired α-stannyl esters **10**. Subsequently, it was found that better yields of products **10** could be obtained by carrying out the enolization of **8** at −42°C. Under these conditions, the use of the hazardous HMPA could be avoided without significant effect on yields. The results are shown in Table 1. Compounds **10** were isolated as viscous liquids and some of them solidified at low temperature (*ca.* −5°C). They are stable to silica gel chromatography and could be stored under nitrogen for several months without appreciable decomposition. No α-silyl α,β-unsaturated esters were detected.

The reaction with enolizable aldehydes gave moderate to good yields of products **10a–d**. The low yield obtained with isobutyraldehyde might be the conse-

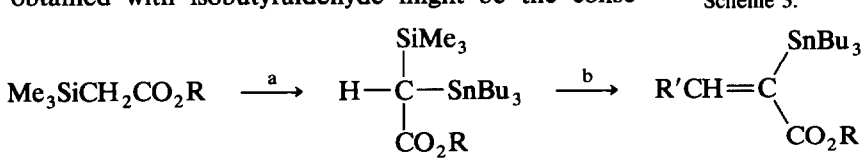
TABLE 1. Reaction of the lithium enolate of tert-butyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)acetate with aldehydes

Aldehyde	R′ in R′CH=C(SnBu$_3$)CO$_2^t$Bu		%Yield [a] (*E*:*Z* ratio) [b]
Butyraldehyde	**10a**	n-C_3H_7	51 (46:54)
Isobutyraldehyde	**10b**	i-C_3H_7	46 (69:31)
Tetradecanal	**10c**	n-$C_{13}H_{27}$	65 (1:1) [c]
Palmitaldehyde	**10d**	n-$C_{15}H_{31}$	44 (1:1) [c]
Benzaldehyde	**10e**		74 (45:55)
p-Tolualdehyde	**10f**		63 (37:63)
p-Chlorobenzaldehyde	**10g**		74 (48:52)

[a] Yields of purified products. [b] Ratio of isomers estimated by HPLC analysis. [c] Ratio of isomers estimated by NMR.



Scheme 3.

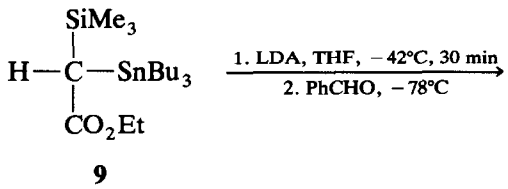


Scheme 2. (a) LDA, THF, −78°C; Bu_3SnCl; (b) LDA, THF, −42°C; R′CHO, −78°C.

quence of steric effects. Aromatic aldehydes afforded good yields of esters **10e–g**. In most reactions, the corresponding destannylated esters **12** were observed as contaminants (Scheme 3). It is likely that these by-products arise from destannylation of **8** *in situ* followed by carbonyl olefination of the α-silyl ester enolate **11** [23]. Indeed, we noted that, even when stored under nitrogen and at low temperature (−5°C), ester **8** decomposed slowly to tert-butyl α-(trimethylsilyl)acetate (**6**) and tin by-products. Not surprisingly, the yield of destannylated esters **12** increased when aged samples of starting ester **8** were used. Optimum yields were secured by employing freshly prepared samples of **8**.

Conceivably, compound **12** could also arise from decomposition of **10**. This could occur either under the basic reaction conditions or during chromatography *via* a protiodestannylation pathway. However, this possibility can be dismissed on the following basis: first, ^{1}H NMR analysis revealed that the destannylated esters **12** were already present in the crude reaction products; second, control experiments showed that protiodestannylation of **10** was minimal during silica gel chromatography; and, third, prolonged reaction times did not increase the yields of by-products **12**.

Only one reaction was carried out using ethyl ester **9**. Generation of the derived lithium enolate followed by addition of benzaldehyde produced compound **13** in 12% yield (eqn. (1)). This result can be explained in terms of the relative lower stability of ethyl ester enolates compared to their tert-butyl ester analogues [24].



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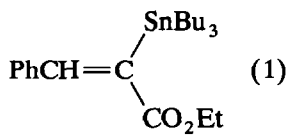
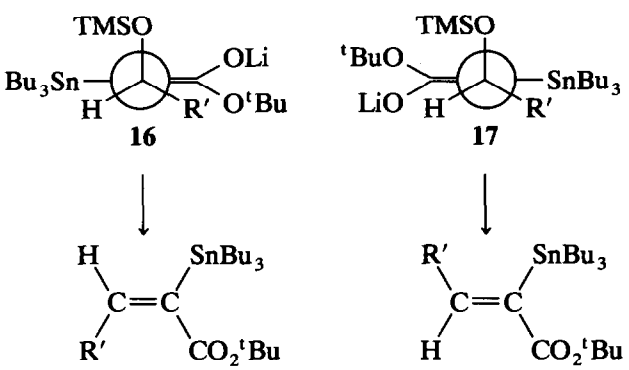


(1)

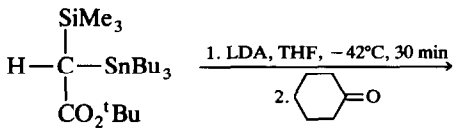
13



16 **17**

Fig. 1.

Cyclohexanone failed to give the expected β,β-disubstituted α-stannyl α,β-unsaturated ester when subjected to this procedure. Treatment of the lithium enolate of **8** with this ketone afforded a 71% yield of tert-butyl cyclohexylideneacetate (**14**) (eqn. (2)). Here again, ^{1}H NMR analysis clearly revealed the presence



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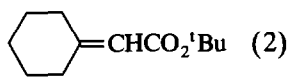
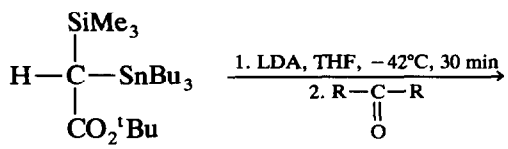


(2)

14

of compound **14** as the major component of the crude reaction product. Therefore, its formation cannot be attributed to protiodestannylation of the expected α-stannylated product during chromatography. On the other hand, the reaction with acetone afforded an inseparable mixture of products. ^{1}H NMR analysis suggested the presence of two major components: the expected α-stannylated alkenoate **15a** and starting ester **8**, each one in approximately 30% yield (eqn. (3)).



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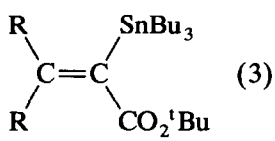


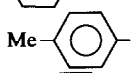
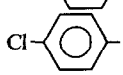
(3)

15a, R = Me
15b, R = Ph

Additionally, the reaction with benzophenone has been reported to give a 46% yield of the desired product **15b** [23]. It is tempting to explain these results by proposing that the anion of **8** tends to act as a base with enolizable ketones. In the case of the more hindered cyclohexanone, destannylation of **8** followed by condensation of the resulting α-silyl ester enolate with the carbonyl compound would give **14**. However, we believed that this rationalization could be an oversimplification of the actual steps involved in this transformation and that further studies are necessary to clarify its mechanism.

The α-stannyl esters **10** were obtained as a mixture of *E*:*Z* isomers whose composition was estimated by ^{1}H NMR and HPLC analyses. Assignment of *E*,*Z* stereochemistry was based on the chemical shifts of the vinylic hydrogens [7] (Table 2).

TABLE 2. tert-Butyl 2-(tri-n-butylstannyl)-2-alkenoates (**10a–g**)

R′ in	$R'CH=C(SnBu_3)CO_2{}^tBu$	^1H NMR [a], −CH=			IR [c], cm^{-1}	
		E	*Z*		C=O	C=C
10a	n-C_3H_7	5.96	7.30	t, J = 7 Hz	1690	1590
10b	i-C_3H_7	5.70	7.00	d, J = 9 Hz	1695	1595
10c	n-$C_{13}H_{27}$	5.90	7.23	t, J = 7 Hz	1700	1590
10d	n-$C_{15}H_{31}$	5.95	7.24	t, J = 7 Hz [b]	1700	1590
10e		6.63	8.26	s	1690	1580
10f		6.60	8.26	s	1690	1595
10g		6.53	8.13	s [b]	1695	1630

[a] Taken in deuterated chloroform as solvent. [b] Taken in carbon tetrachloride as solvent. [c] Taken as neat samples.

It is reasonable to assume that the reaction proceeds through the proposed stepwise elimination mechanism shown in Scheme 1. Then, the low stereoselectivity observed for the formation of **10** could be attributed to the similar stabilities of conformations **16** and **17** [25*], from which elimination of the trimethylsilyloxy group should occur (Fig. 1).

In conclusion, a preparative method for the synthesis of α-stannyl α,β-unsaturated esters, which provides moderate to good yields of products as a mixture of *E*, *Z* isomers, has been developed. While it is possible to obtain a wide variety of β-substituted esters, the method is not applicable to enolizable ketones.

3. Experimental details

All reactions were run under dry nitrogen. Flash chromatography was carried out according to Still [26]. Analytical thin-layer chromatography was performed using Merck 60 F-254 precoated silica gel glass plates (0.25 mm layer thickness). Preparative thin-layer chromatography was performed using Merck PF254-360 precoated silica gel plates (2 mm layer thickness). Analytical high pressure liquid chromatography (HPLC) was performed using a Varian Model 5000 equipped with a Micropak Si-5 column. Infrared spectra were recorded on Perkin Elmer 567 or 753B spectrophotometers. Proton NMR spectra were recorded on a Varian T-60 or a Varian XL-100 spectrometer. For compounds containing a trimethylsilyl group, chemical shifts are reported in parts per million (δ) downfield from this group; otherwise, chemical shifts are reported downfield from tetramethylsilane. Combustion analyses were carried out using a Perkin Elmer 240 Elemental Analyzer. LDA solutions were prepared in the following way: diisopropylamine (10% molar excess) was added dropwise to a commercial solution of known concentration of *n*-butyllithium in hexanes at 0°C. After 10 min, the solvent was evaporated *in vacuo* and the residual white solid was dissolved in enough THF to obtain a *ca.* 1 M solution.

3.1. *tert-Butyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)-acetate (8)*

To a solution of LDA (43 mmol) at −78°C was added dropwise a solution of tert-butyl α-(trimethylsilyl)acetate (**6**) [13] (7.18 g, 38.1 mmol) in THF (10 ml). After 20 min, tri-n-butyltin chloride (10.77 ml, 38.13 mmol) was added and stirring was continued for 20 min at −78°C. Then, the reaction mixture was poured into saturated aqueous ammonium chloride (50 ml) and extracted with ether (3 × 50 ml). The combined organic extracts were washed with saturated aqueous sodium chloride (50 ml), dried (Na_2SO_4) and concentrated to give 17.3 g of ester **8** *ca.* > 90% pure by ^1H NMR. Flash chromatography (hexanes : dichloromethane 85 : 15) afforded 13.6 g (75%) of ester **8**: IR (neat) 1680 cm^{-1} (C=O); ^1H NMR (60 MHz, CCl_4) δ 1.5 (s, 1H, CHSiSn), 1.3 (s, 9H, $-OC(CH_3)_3$), 1.5–0.7 (m, 27H, $-Sn(C_4H_9)_3$), 0.0 (s, 9H, $-Si(CH_3)_3$). Anal. Found: C, 53.10; H, 9.98. $C_{21}H_{46}O_2SiSn$ calcd.: C, 52.83; H, 9.71%.

3.2. *Ethyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)acetate (9)*

To a solution of lithium dicyclohexylamide (LDCA, 5.0 mmol prepared from dicyclohexylamine, 6.0 mmol, and n-butyllithium, 3.1 ml of a 1.6 M solution in hexane) in THF (25 ml) at −78°C was added dropwise

* Reference number with an asterisk indicates a note in the list of references.

ethyl α-(trimethylsilyl)acetate (**7**) [27] (0.84 ml, 4.6 mmol). After 30 min, tri-n-butyltin chloride was added (1.3 ml, 4.6 mmol) and stirring was continued for 30 min at −78°C. The reaction mixture was poured into petroleum ether (40–60°C) and washed with aqueous citric acid 0.1 M (2 × 50 ml), water (2 × 50 ml), aqueous $NaHCO_3$ 0.1 M (2 × 50 ml) and water (2 × 50 ml). The organic layer was separated, dried (Na_2SO_4) and concentrated. Flash chromatography of the residual liquid hexanes : dichloromethane 75 : 25) afforded 0.4746 g (23%) of ester **9**: IR (neat) 1680 cm^{-1} (C=O); ^1H NMR (60 MHz, CCl_4) d 3.9 (q, 2H, $J = 7$ Hz, $-OCH_2-$), 1.53 (s, 1H, −CHSiSn), 1.70–0.60 (m, 30H, $-Sn(C_4H_9)_3$ and CH_3), 0.0 (s, 9H, $Si(CH_3)_3$).

3.3. α-(Tri-n-butylstannyl)-α,β-unsaturated esters (10)

The general procedure was as follows. To a solution of LDA (1.1 mmol) and hexamethylphosphoramide (HMPA) (2.2 mmol) in THF at −78°C was added, dropwise and with stirring, a solution of tert-butyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)acetate (**8**) (0.4774 g, 1.0 mmol) in THF (3 ml). The dry ice-acetone bath (−78°C) was replaced by a dry ice-acetonitrile bath (−42°C) and the reaction mixture was stirred at the latter temperature for 20 min. After recooling to −78°C, the aldehyde compound (1.0 mmol) was added. After 10 min, the reaction mixture was poured into hexanes (25 ml) and washed sequentially with saturated aqueous ammonium chloride (2 × 25 ml) and water (2 × 25 ml). The organic layer was dried (Na_2SO_4) and concentrated.

The purification procedure, $E:Z$ ratio, yield, and spectroscopic and analytical data corresponding to each product are reported below.

3.4. tert-Butyl 2-(tri-n-butylstannyl)-2-hexenoate (10a)

This product was obtained as a 46:54 $E:Z$ mixture in 51% yield after purification by flash chromatography (12% dichloromethane in hexanes): IR (neat) 1690 cm^{-1} (C=O), 1590 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.3 and 5.96 (t, 1H, $J = 7$ Hz, HC=C, Z and E isomers respectively), 2.3 (m, 2H, $C=C-CH_2$), 1.5 (s, 9H, $-OC(CH_3)_3$), 1.7–0.70 (m, 32H, $Sn(C_4H_9)_3$ and CH_2CH_3). Anal. Found: C, 57.88; H, 9.54. $C_{22}H_{44}O_2Sn$ calcd.: C, 57.53; H, 9.67%.

3.5. tert-Butyl 2-(tri-n-butylstannyl)-4-methyl-2-pentenoate (10b)

This product was obtained as a 69:31 $E:Z$ mixture in 46% yield after purification by flash chromatography (12% dichloromethane in hexanes): IR (neat) 1695 cm^{-1} (C=O), 1595 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.0 and 5.7 (d, 1H, $J = 9$ Hz, HC=C, Z and E isomers respectively), 3.10 (m, 1H, C=C–CH), 1.50 (s, 9H, $-OC(CH_3)_3$), 1.70–0.60 (m, 33H, $-Sn(C_4H_9)_3$ and $-C(CH_3)_2$). Anal. Found: C, 57.21; H, 9.56. $C_{22}H_{44}O_2Sn$ calcd.: C, 57.33; H, 9.67%.

3.6. tert-Butyl 2-(tri-n-butylstannyl)-2-hexadecenoate (10c)

This product was obtained as a 1:1 $E:Z$ mixture in 65% yield after purification by flash chromatography (10% dichloromethane in hexanes): IR (neat) 1700 cm^{-1} (C=O), 1590 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 7.23 and 5.89 (t, 1H, $J = 7$ Hz, HC=C, Z and E isomers respectively), 2.6–1.82 (m, 2H, $C=C-CH_2-$), 1.6–0.73 (m, 52H, $-Sn(C_4H_9)_3$ and $CH_3-(CH_2)_{11}-$), 1.50 (s, 9H, $-OC(CH_3)_3$). Anal. Found: C, 63.93; H, 10.59. $C_{32}H_{64}O_2Sn$ calcd.: C, 64.11; H, 10.76%.

3.7. tert-Butyl 2-(tri-n-butylstannyl)-2-octadecenoate (10d)

This product was obtained as a 1:1 $E:Z$ mixture in 44% yield after purification by flash chromatography (10% dichloromethane in hexanes): IR (neat) 1700 cm^{-1} (C=O), 1590 cm^{-1} (C=C); ^1H NMR (60 MHz, CCl_4) δ 7.24 and 5.95 (t, 1H, $J = 7$ Hz, HC=C, Z and E isomers respectively), 2.30–0.70 (m, 58H, $-Sn(C_4H_9)_3$ and $CH_3-(CH_2)_{14}-$), 1.50 (s, 9H, $-OC(CH_3)_3$). Anal. Found: C, 65.20; H, 11.05. $C_{34}H_{68}O_2Sn$ calcd.: C, 65.07; H, 10.92%.

3.8. tert-Butyl α-(tri-n-butylstannyl) cinnamate (10e)

This product was obtained as a 45:55 $E:Z$ mixture in 74% yield after purification by flash chromatography (30% dichloromethane in hexanes): IR (neat) 1690 cm^{-1} (C=O), 1580 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 8.26 and 6.63 (s 1H, HC=C, Z and E isomers respectively), 7.23 (s, 5H, Ph), 1.53 and 1.40 (s, 9H, $-OC(CH_3)_3$, Z and E isomers respectively), 1.70–0.70 (m, 27H, $-Sn(C_4H_9)_3$). Anal. Found: C, 61.24; H, 8.38. $C_{25}H_{42}O_2Sn$ calcd.: C, 60.87; H, 8.58%.

3.9. tert-Butyl 2-(tri-n-butylstannyl)-3-(4-methylphenyl)-2-propenoate (10f)

This product was obtained as a 37:63 $E:Z$ mixture in 63% yield after purification by preparative TLC (25% dichloromethane in hexanes): IR (neat) 1690 cm^{-1} (C=O), 1595 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 8.26 and 6.60 (s, 1H, HC=C, Z and E isomers respectively), 7.16 (s, 4H, aromatic), 2.36 (s, 3H, CH_3), 1.55 and 1.46 (s, 9H, $-OC(CH_3)_3$, Z and E isomers respectively), 1.70–0.70 (m, 27H, $-Sn(C_4H_9)_3$). Anal. Calcd. for $C_{26}H_{44}O_2Sn$: C, 61.56; H, 8.74. Found: C, 61.73; H, 8.75%.

3.10. tert-Butyl 2-(tri-n-butylstannyl)-3-(4-chlorophenyl)-2-propenoate (10g)

This product was obtained as a 48:52 $E:Z$ mixture in 74% yield after purification by preparative TLC

(50% dichloromethane in hexanes): IR (neat) 1695 cm^{-1} (C=O), 1630 cm^{-1} (C=C); ^1H NMR (60 MHz, CCl_4) δ 8.13 and 6.53 (s, 1H, HC=C, *Z* and *E* isomers respectively), 7.26 (s, 4H, aromatic), 1.53 and 1.40 (s, 9H, $-OC(CH_3)_3$, *Z* and *E* isomers respectively), 1.70–0.70 (m, 27H, $-Sn(C_4H_9)_3$). Anal. Found: C, 57.16; H, 7.82. $C_{25}H_{41}O_2Sn$ calcd.: C, 56.90; H, 7.83%.

3.11. Ethyl α-(tris-n-butylstannyl) cinnamate (13)

To a solution of LDA (10 mmol) in THF at −78°C was added dropwise a solution of ethyl α-(tri-n-butylstannyl)-α-(trimethylsilyl)acetate (**9**) (0.4628 g, 1.00 mmol) in THF (2 ml). The dry ice-acetone bath (−78°C) was replaced by a dry ice-acetonitrile bath (−42°C) and the reaction mixture was stirred at the latter temperature for 30 min. After recooling to −78°C, benzaldehyde (0.05 ml, 0.5 mmol) was added. After 10 min, the reaction mixture was poured into hexanes (25 ml) and washed with water (2 × 50 ml). The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography (25% dichloromethane in hexanes) of the residual liquid afforded 0.0270 g (12%) of ester **11**: IR (neat) 1700 cm^{-1} (C=O), 1580 cm^{-1} (C=C); ^1H NMR (60 MHz, $CDCl_3$) δ 8.34 and 6.70 (s, 1H, HC=C, *Z* and *E* isomers respectively), 7.31 (s, 5H, aromatic), 4.20 (m, 2H, $-OCH_2-$), 1.70–0.60 (m, 30H, $-Sn(C_4H_9)_3$ and CH_3). Anal. Found: C, 59.17; H, 8.39. $C_{23}H_{38}O_2Sn$ calcd.: C, 59.38; H, 8.23%.

3.12. tert-Butyl cyclohexyledeneacetate (14)

The general procedure for the preparation of esters **10** described above was followed. Cyclohexanone was used as the carbonyl compound to afford 0.1331 g (71%) of ester **14**: IR (neat) 1700 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^1H NMR (60 MHz, CCl_4) δ 5.43 (broad s, 1H, HC=C), 2.78 (m, 2H, CH_2–C=C *cis* to carboalkoxy group), 2.10 (m, 2H, CH_2–C=CH, *trans* to carboalkoxy group), 1.60 (m, 6H, $-(CH_2)_3-$), 1.40 (s, 9H, $-OC(CH_3)_3$).

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