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Some Chemistry of Organotin Synthons containing Two Organotin Moieties

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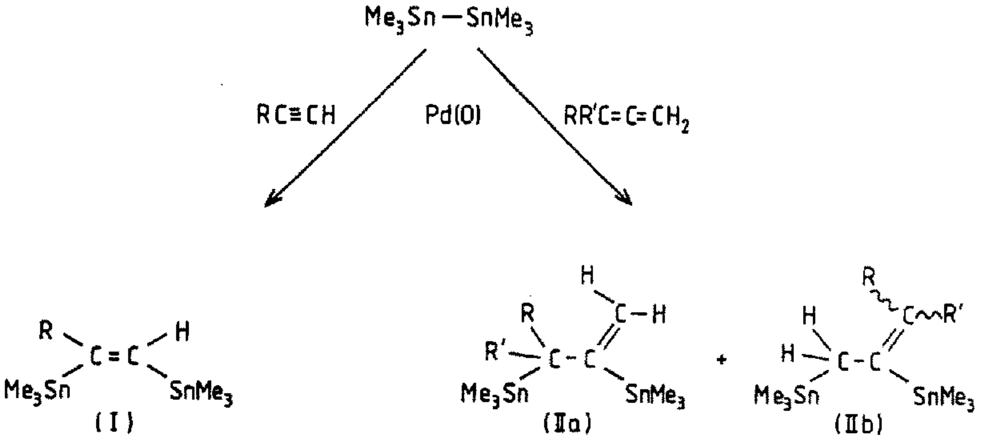
Abstract

A series of reactions are described for two bifunctional organotin synthons, 1,2- and 2,3-bis(trimethylstannyl)-1-alkenes. These reactions include bromodemethylation at tin, lithiodestannylation and palladium-catalysed C-C bond formation; while the former synthon appears extremely promising as a synthetic reagent, the latter has limitations due to its tendency to decomposition.

Introduction

Although organotins are widely used in organic synthesis[1], molecules containing two organotin moieties have so far been virtually ignored. Reich[2] has described a number of reactions of a molecule which can exist as either 1,4-bis(trimethylstannyl)-2-butyne or 2,3-bis(trimethylstannyl)-buta-1,3-diene, while we have previously prepared and studied 1,1-bis(trimethylstannyl)-1-alkenes[3]. Palladium-catalysed addition of hexamethylditin to 1-alkynes[4] or allenes[5] yields molecules I and II which appeared to have considerable synthetic potential, and we report here some initial investigations on the chemistry of these compounds.



Results and Discussion

a) 2-Bis(trimethylstannyl)-1-alkenes (I)*

Compounds of this type are readily available from the addition of hexamethylditin to 1-alkynes using tetrakis(triphenylphosphine)-palladium as catalyst; hexaethyl- and hexabutylditin, however, do not react quantitatively[4]. The sole product is normally the Z-isomer, though photochemical isomerisation to give the E-isomer can often be observed.

i) Functionalisation of organotin moieties in (I)

Bromodemethylation at tin can be readily carried out using Me_2SnBr_2[3,7] or Me_3SnBr[8]. In the present compounds the selectivity of this reaction does not permit a clean reaction at only one trimethyltin centre, but double bromodemethylation of either Z- or E-(I) is readily possible using either Me_2SnBr_2 or Me_3SnBr. Except for Z-bis(trimethylstannyl)-ethene itself [(I), R=H],for which formation of 40% E-product was observed, no isomerisation was observed during the bromodemethylation of the Z-isomers, and the yields were moderate to good (56-81%). The E-isomers underwent bromodemethylation with similar yields(61-84%). We also observed that it is possible to photoisomerise the doubly bromodemethylated Z-isomer derived from (I), R=$MeOCH_2$ completely to the corresponding E-isomer by UV-irradiation for 96h in cyclohexane as solvent.

$$\text{Z- (or E)- }RC(SnMe_3)=CHSnMe_3 + 2\ Me_2SnBr_2\ \text{(or 2 }Me_3SnBr)$$
$$\longrightarrow \text{Z- (or E)- }RC(SnMe_2Br)=CHSnMe_2Br + 2\ Me_3SnBr\ \text{(or }Me_4Sn)$$

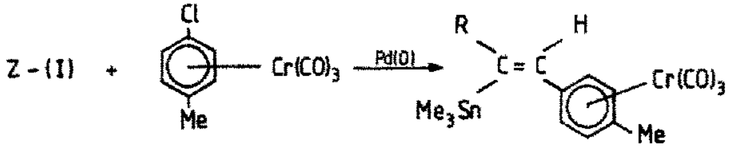
ii) Palladium-catalysed carbon-carbon bond formation

The use of vinyl- and allyltin compounds in palladium-catalysed carbon-carbon bond formation is by now well-known[9], and the 1,2-distannyl-1-alkenes, as stable discrete difunctional moieties, provide a considerable synthetic potential in stereospecific olefin formation. We find that it is indeed possible to carry out regiospecific coupling reactions using allylic, benzylic or aromatic halides in the presence of $PhCH_2PdCl(PPh_3)_2$, the tin on carbon atom 1 being replaced selectively.

Allyl and benzyl bromide react with Z-(I), R = Ph, $MeOCH_2$, MeCH(OH), in refluxing benzene as solvent; it is advisable to take a slight excess of the organotin compound in order to obtain a completely clean reaction. However, purification of the products by distillation is not possible because of their tendency to polymerisation, and we are at present working on a modification of the reaction procedure.

$$\text{Z-(I)} + R\text{-}X \longrightarrow \text{Z-}RC(SnMe_3)=CHR + Me_3SnX$$
$$(R = CH_2{=}CHCH_2,\ PhCH_2;\ X = Br)$$

Attempts to use the same catalyst to induce a reaction with bromobenzene were unsuccessful, so that for the introduction of a phenyl residue we resorted[10] to the method described recently by Scott[11], who reacted aryltricarbonylchromium complexes with tetraorganotins in the presence of Pd(0) catalyst. We find that an aryltricarbonylchromium complex (aryl = p-chlorotoluene) reacts regio- and stereospecifically with Z-(I), R = Ph, $MeOCH_2$, MeCH(OH), $Me_2C(OH)$, in the presence of $Pd(PPh_3)_4$ to give 1-[(tricarbonyl-chromium)aryl]-2-trimethylstannyl-1-alkenes (aryl = p-tolyl) in yields of 34-85% (reaction time ca. 22 h, temp. ca. 70°C, solvent THF).



iii) Halodestannylation

While geminal distannylalkenes do not react cleanly with halogens, they react with N-bromosuccinimide in a 1:1 molar ratio to give stannylated vinyl bromides; these consist mainly of the E-isomers[12]. The vicinal Z-distannylalkenes (I), however, are cleaved regioselectively by iodine, whereby the tin at carbon atom 1 is removed. Even bromine gives a relatively clean reaction, though small amounts of dibromoalkenes are obtained as by-products. A selective bromodestannylation is afforded by N-bromosuccinimide. The stannylated vinyl halides, which are in each case stereochemically pure Z-isomers, can be purified by distillation.

$$\text{Z-RC(SnMe}_3\text{)=CHSnMe}_3 + \text{X-Y} \longrightarrow \text{RC(SnMe}_3\text{)=CHX} + \text{Me}_3\text{SnY}$$

$$\text{(R = MeOCH}_2\text{, Me}_2\text{NCH}_2\text{, Ph, MeCH(OH), Me}_2\text{C(OH); X-Y = Br}_2\text{, I}_2\text{, NBS)}$$

In contrast, the behaviour of the E-isomers is more complex. They can undergo decomposition when treated with halogen or NBS: reaction of E-(I) (R = H, $MeOCH_2$) with iodine or NBS led to the formation of the alkyne RC=CH and either trimethyltin iodide or a mixture of trimethyltin bromide and N-trimethylstannylsuccinimide. On the other hand, treatment of (I), R = $MeOCH_2$, with bromine led to formation of a distannylalkene in which the trimethylstannyl group on carbon 1 had undergone bromode*methyl*ation; this is very reminiscent of the reaction reported recently by Jousseaume[12] and must also involve intramolecular chelation of the tin atom.

$$\text{E-RCH(SnMe}_3\text{)=CHSnMe}_3 + \text{X-Y} \longrightarrow \text{RC=CH} + \text{Me}_3\text{SnX} + \text{Me}_3\text{SnY}$$

$$\text{(R = H, MeOCH}_2\text{; X-Y = I}_2\text{, NBS)}$$

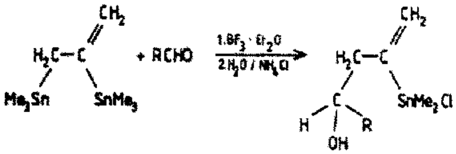
$$\text{E-MeOCH}_2\text{C(SnMe}_3\text{)=CHSnMe}_3 + \text{Br}_2 \longrightarrow \text{E-MeOCH}_2\text{C(SnMe}_3\text{)=CHSnMe}_2\text{Br} + \text{MeBr}$$

b) 2,3-Bis(trimethylstannyl)-1-alkenes[14]

These are prepared by palladium-catalysed addition of hexamethylditin to allenes[5]; at least in the case of allene itself, hexaethyl- and hexabutylditin also add quantitatively (for details see experimental section). The kinetic (low-temperature) product is (IIa), while at higher temperatures or on heating (IIa) in the presence of the catalyst (IIb) is formed; the latter can in the general case exist as a Z/E isomer mixture. In order to discover reactivity patterns without dealing with isomer mixtures, we have so far concentrated our investigations on the prototype compound, 2,3-bis(trimethylstannyl)-1-propene, referred to below as (II); the latter is also obtained when propyne and Me_6Sn_2 are allowed to react in the presence of $Pd(PPh_3)_4$[5].

i) Addition to aldehydes

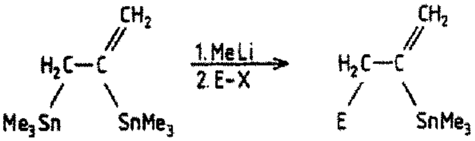
Here the expected selectivity is observed; reaction with propionaldehyde or benzaldehyde yields the corresponding allylic alcohol. However, during workup the second tin centre is surprisingly functionalised by chlorodemethylation; this presumably again involves intramolecular coordination of the OH function to the tin centre. The products are colourless solids which undergo decomposition on attempted distillation and cannot readily be freed from polymeric by-products; they have therefore as yet only been characterised by NMR spectroscopy.



The symmetrical nature of the starting material does not permit the observation of allylic inversion, which thus still remains to be demonstrated for this type of substrate.

ii) Lithiodestannylation

The conversion of organotins to organolithiums is of not only historical but also of great synthetic interest. Again the selectivity of the reaction is a potential problem, but because of the different reactivities of the allylic and vinylic tin moieties we hoped that a quantitative or at least semiquantitative monolithiodestannylation would occur, as is the case for 1,1-distannyl-1-alkenes[15]. Lithiodestannylation of (II) in fact occurred as expected at the allylic tin centre, and the anion so obtained was allowed to react with a number of electrophiles.



(E-X = H_2O, Me_2SO_4, Me_3SiCl, Me_3GeCl, Me_3PbCl, Me_2CO, PhCOMe, MeCHO, EtCHO, PhCHO, $CH_2{=}CHCH_2Br$, $PhCH_2Br$, $PhCH{=}CHCH_2Br$, $MeCH{=}CHCH_2Cl$)

Isolated yields of products were only moderate (23–64%), though spectroscopically determined yields were generally much better. The vinyltin products were generally stable towards heat and light, even the stannyl-plumbyl alkene being distillable. However, this compound decomposes on standing under argon to give a brown viscous oil. The allylic alcohol resulting from the reaction with acetophenone undergoes decomposition during distillation. Attempts to react the organolithium species with acid chlorides and carbon dioxide were unsuccessful.

iii) Attempted halodestannylation

In contrast to the 1,2-distannyl-1-alkenes, which undergo selective cleavage of trimethylstannyl groups by halogens or N-bromosuccinimide, the 2,3-distannyl-1-propene system undergoes complete cleavage by bromine or iodine to yield allene and the trimethyltin halide. N-Bromosuccinimide causes the formation of trimethyltin bromide and an intractable polymeric material.

iv) Attempted palladium-catalysed coupling

Reactions of (II) with allyl,benzyl, crotyl and cinnamyl bromides as well as allyl acetate in the presence of $PhCH_2PdCl(PPh_3)_2$ lead to the formation of trimethyltin bromide (or acetate), allyl-, benzyl-, crotyl- or cinnamyltrimethyltin and (presumably) allene. No reaction occurs in the absence of the catalyst, while under the reaction conditions (II) is decomposed by the catalyst to give hexamethylditin, which is presumably the source of the organotin products obtained.

Experimental

All air-sensitive compounds were handled under an argon atmosphere. NMR spectra were recorded using a Varian EM360 (^1H, 60 MHz) or a Bruker AM-300 spectrometer (^1H, 300 MHz; ^{13}C, 75.43 MHz; ^{119}Sn, 111.82 MHz, ^{207}Pb, 62.77 MHz). The internal standards used were TMS (^1H, ^{13}C), Me_4Sn (^{119}Sn) and Me_4Pb (^{207}Pb). While complete NMR data were recorded, only selected data typical of the compounds are reported here in Tables 1 and 2. New compounds gave satisfactory elemental analyses. Organotin synthons (I) and (II) were prepared as described previously[4,5].

General Procedure for Bromodemethylation of (I)

A mixture of 10 mmol (I) and dimethyltin dibromide (6.2g, 20 mmol) was heated without solvent at 60-65°C for 15 h. In most cases a white or brown solid separated: the mixture was then treated with n-hexane and the solid centrifuged off. The hexane solution, or the reaction mixture when no solid had separated, was freed from volatile materials (hexane was removed using a rotary evaporator, trimethyltin bromide at the oil pump), leaving the product as an oil or a solid. Solids were recrystallised from cyclohexane.

In an alternative procedure (I) (5 mmol) and trimethyltin bromide (2.4 g, 10 mmol) were stirred at room temperature for 72 h. Tetramethyltin was removed using a rotary evaporator, leaving the product which was if necessary recrystallised from cyclohexane.

The yields and melting points of the products derived from Z- and E-(I) were as follows:

Z-(I): R = H, 56% (oil); R = Ph, 65% (oil); R = MeCH(OH), 74%, 84°C; R = $MeOCH_2$, 65%, 74°C; R = $Me_2C(OH)$, 63%, 126°C.

E-(I): R = H, 62%, 105°C; R = Ph, 61%, 94°C; R = EtOOC, 84%, 97°C.

For NMR data see Table 1.

The product derived from Z-(I), R=$MeOCH_2$ (1.68 g, 3 mmol) was dissolved in cyclohexane (10 mL) and irradiated for 96 h using a high-pressure mercury lamp (TQ 150, Heraeus, Hanau). NMR analysis of the product (m.p. 100°C) indicated its complete conversion to the E-isomer.

General Procedure for Pd-catalysed Coupling using (I)

Z-(I) (10 mmol) was dissolved in benzene (20 mL); the organic halide (10 mmol) and the catalyst $PhCH_2PdCl(PPh_3)_4$ (ca. 0.5 mmol) were added and the reaction mixture heated at 80°C for 15 h. The solvent was removed using a rotary evaporator, and trimethyltin bromide at the oil pump. Attempts to distil the products lead to polymerisation, and they were characterised by their NMR spectra (see Table 1).

Coupling of Z-(I) with an arylchromiumtricarbonyl complex

The tricarbonylchromium complex was prepared from 4-chlorotoluene and chromium hexacarbonyl as described previously[16,17]. p-Chloro-toluenetricarbonylchromium (2.0 g, 7.3 mmol) and Z-(I) (7.3 mmol) were dissolved in THF (50 mL) and treated with $Pd(PPh_3)_4$ (ca. 0.05 mmol). The mixture was stirred at 70°C in the dark for 22 h, allowed to cool to room temperature and filtered through a small quantity of silica gel. THF was distilled off at room temperature under reduced pressure and the products characterised by NMR spectroscopy. The following yields were determined by integration of peak intensities in the proton spectra: R = Ph, 70%; R = $MeOCH_2$, 62%; R = MeCH(OH), 34%; R = $Me_2CH(OH)$, 85%. NMR data are given in Table 1.

Halodestannylation of Z-(I)

Z-(I) (10 mmol) in methylene chloride (25 mL) was treated at -78°C with a solution of bromine, iodine or N-bromosuccinimide (10 mmol) in methylene chloride (100 mL, 25 mL for bromine). The reaction mixture was stirred for 1 h and allowed to warm to room temperature. The solvent was distilled off at normal pressure. In the case of the halogens the trimethyltin halide was then distilled off at the water pump, while for NBS the residue was treated with ether (30 mL) and the insoluble N-stannylsuccinimide filtered off. In all cases purification was effected by distillation. Yields and boiling points were as follows:

R	reagent	yield(%)	b.p.(°C/mm Hg)
$MeOCH_2$	Br_2/NBS	90/75	56/0.02
$MeOCH_2$	I_2	85	104/0.001
Me_2NCH_2	Br_2/NBS	78/83	68/0.1
Me_2NCH_2	I_2	70	70/0.005
Ph	Br_2/NBS	41/58	108/0.001
Ph	I_2	83	115/0.001
MeCH(OH)	I_2	78	89/0.005
MeCH(OH)	NBS	73	73/0.001
$Me_2CH(OH)$	I_2	48	92/0.001
$Me_2CH(OH)$	NBS	43	83/0.001

For spectral data of the products see Table 1.

Reactions of E-(I) with Halogens and N-Bromosuccinimide

These were carried out as described for the Z-isomers; trimethyltin halide and alkyne were formed quantitatively except for R = $MeOCH_2$, in the case of which $RCH(SnMe_3)=CHSnMe_2Br$ was isolated by distillation (yield 52%, b.p. 135°C/0.15 mm Hg); for its NMR data see Table 1.

Table 1

Selected NMR Data for Compounds of the Type Z/E-CHX=CRSnMe$_2$Y

X	Z/E	R	Y	δ(=CH)	δ(=CH)	δ(=CSnMe$_2$X)	δ(=CSnMe$_2$X)
SnMe$_2$Br	Z	H	Br	7.57(269)	155.0(37)	155.0(492)	a
SnMe$_2$Br	E	H	Br	7.23(154)	152.9(37)	152.9(409)	47.3(1516)
SnMe$_2$Br	Z	Ph	Br	7.53(239)	147.4(66)	167.5(483)	19.9(598)
SnMe$_2$Br	E	Ph	Br	7.31(120)	145.6(47)	168.7(396)	40.8(1326)
SnMe$_2$Br	Z	MeOCH$_2$	Br	7.26(280)	144.1(64)	165.2(490)	14.1(665)
SnMe$_2$Br	Z	MeCH(OH)	Br	7.13(284)	140.0(69)	172.8(487)	14.6(695)
SnMe$_2$Br	Z	Me$_2$C(OH)	Br	7.07(286)	137.2(69)	177.5(508)	12.6(715)
SnMe$_2$Br	E	EtOOC	Br	8.34(112)	170.1(47)	154.7(401)	40.4(946)
CH$_2$CH=CH$_2$	Z	Ph	Me	6.23(132)	136.5(25)	146.8(437)	-46.4
CH$_2$CH=CH$_2$	Z	MeOCH$_2$	Me	6.15(132)	139.7(25)	142.8(450)	-47.8
CH$_2$CH=CH$_2$	Z	MeCH(OH)	Me	6.05(133)	138.0(25)	150.8(445)	-53.7
PhCH$_2$	Z	Ph	Me	7.18(132)	142.1(25)	146.6(144)	-46.0
PhCH$_2$	Z	MeOCH$_2$	Me	7.15(133)	140.9(25)	142.6(445)	-47.3
PhCH$_2$	Z	MeCH(OH)	Me	7.32(131)	142.1(25)	146.6(442)	-53.7
4-MeC$_6$H$_4$Cr(CO)$_3$	Z	Ph	Me	6.83(120)	138.4(19)	152.1(388)	-38.5
4-MeC$_6$H$_4$Cr(CO)$_3$	Z	MeOCH$_2$	Me	6.81(120)	136.6(14)	148.9(383)	-41.5
4-MeC$_6$H$_4$Cr(CO)$_3$	Z	MeCH(OH)	Me	6.77(*)	133.1(15)	157.5(408)	-48.5
4-MeC$_6$H$_4$Cr(CO)$_3$	Z	Me$_2$C(OH)	Me	6.72(a)	132.4(14)	162.9(369)	-54.6
Br	Z	Ph	Me	6.88(98)	116.6(31)	149.7(399)	-25.4
Br	Z	MeOCH$_2$	Me	6.81(96)	117.2(22)	154.3(390)	-20.9
Br	Z	MeCH(OH)	Me	6.85(99)	114.9(33)	157.3(398)	-29.5
Br	Z	Me$_2$C(OH)	Me	6.83(104)	113.7(25)	160.9(412)	-29.2
Br	Z	Me$_2$NCH$_2$	Me	6.78(100)	115.1(23)	152.1(426)	-25.2
I	Z	Ph	Me	7.03(112)	91.3(29)	147.2(402)	-11.4
I	Z	MeOCH$_2$	Me	7.04(109)	90.1(37)	158.6(411)	-16.4
I	Z	MeCH(OH)	Me	7.03(114)	88.2(36)	161.5(439)	-16.6
I	Z	Me$_2$C(OH)	Me	6.98(119)	86.7(29)	169.2(425)	-18.8
I	Z	Me$_2$NCH$_2$	Me	6.88(114)	88.3(29)	161.5(439)	-16.6
SnMe$_2$Br	E	MeOCH$_2$	Me	6.46(145)	140.0(11)	159.1(364)	-41.2(1206)

Values in parentheses are those for ^3J(Sn,H), ^2J(Sn,C), ^1J(Sn,C) and ^3J(Sn,Sn) respectively, where Sn refers to ^{119}Sn. Chemical shifts in ppm w.r.t. TMS or Me$_4$Sn, coupling constants in Hz.

* not determined.

Preparation of (II)

Allene is passed through hexamethylditin (15.7 g, 48 mmol) containing tetrakis(triphenylphosphine)-palladium (0.05 g, 0.04 mmol) for 1.5 h, the reaction mixture being kept at 75°C. After this time, the ditin is completely consumed. Distillation affords 16.2 g (92%) of (II), b.p. 43°C/0.005 mm Hg. Analogous reactions of hexaethyl- and hexabutylditin proceed in 89% and 61% yield respectively, the products boiling at 103°C/0.001 mm Hg and 175-179°C/0.05 mm Hg respectively.

Reactions of (II) with aldehydes

The aldehyde (20 mmol) was dissolved in methylene chloride (40 mL) and the solution cooled to −78°C. Boron trifluoride etherate (5.6 g, 40 mmol) was added during 5 min, and a solution of (II) (7.4 g, 20 mmol) in methylene chloride (40 mL) then added dropwise. After 30 min the mixture was allowed to warm to room temperature; it was shaken with cold NH_4Cl solution, the organic phase separated, dried, the solvent removed using a rotary evaporator, and trimethyltin chloride distilled off at the water pump. The allylic alcohol, generally a colourless solid, underwent decomposition on attempted distillation; it was contaminated with polymeric by-products, and yields were 45–55%. Products were characterised by NMR spectroscopy (see Table 2).

Lithiodestannylation of (II) and reaction of the vinyllithium with electrophiles: General Procedure

A solution of methyllithium (20 mmol) in THF (15 mL) was cooled to −78°C and treated with (II) (7.5 g, 20 mmol); the reaction mixture became light green. After 30 min the electrophile (20 mmol) was added; a colour change usually occurred on its addition. The mixture was stirred for a further 30 min and allowed to warm to room temperature. Water (10 mL) was added, the THF solution dried and the THF removed at a rotary evaporator. The products were separated by distillation. Yields and boiling points were as follows:

Electrophile	yield(%)	b.p.(°C/mm Hg)
H_2O	30	30/14
Me_2SO_4	42	40/14
Me_3SiCl	64[a]	75-80/14
Me_3GeCl	35	83-91/14
Me_3PbCl	23	105-115/14
Me_2CO	38	44-48/0.7
PhCOMe	41	120/0.005
MeCHO	44	36-40/0.005
EtCHO	47	73/0.001
PhCHO	48	95-105/0.005
$CH_2=CHCH_2Br$	39	77-80/14
$PhCH_2Br$	44	80-86/0.05
$PhCH=CHCH_2Br$	45	94-102/0.005
$MeCH=CHCH_2Cl$	52	30-31/0.01
$HC{\equiv}CCH_2Br$	40[b]	70-85/0.05

[a] In other solvents (ether, glyme, TMED) yields were lower; [b] product contains ca. 5% of the allenyl isomer.

Attempted halodestannylation of (II)

(II) (5.6 g, 15 mmol) was dissolved in the appropriate solvent (CH_2Cl_2 (35 mL) for reactions with iodine and NBS, methanol (35 mL) for reactions with bromine) and the solution cooled to −78°C. The halogen reagent (15 mmol), dissolved in the same solvent, was added during 1 h. The reaction mixture was allowed to warm to room temperature. In the case of bromine and iodine the solvent was pumped into a cold trap and shown by IR, GLC and proton NMR to contain allene; the residue consisted of trimethyltin bromide. In the case of NBS the solvent was removed using a rotary evaporator and the residue taken up in ether (30 mL): N-trimethylstannyl succinimide crystallised out from the resulting solution on standing at 0°C. It was filtered off and the ether removed from the filtrate, leaving trimethyltin bromide contaminated with a little stannyl succinimide.

Table 2

Selected NMR Data for Compounds of the Type XCH$_2$C(SnMe$_2$Y)=CH$_2$

X	Y	δ(CH$_2$X)	δ(CH$_2$X)	δ(CSn)	δ(CSn)	δ(=CH$_2$)	δ(=CH$_2$)
MeCH(OH)	Cl	2.26	46.5(63.6)	149.6(648.5)	-20.8	5.84(102),5.94(216)	128.2(35.6)
EtCH(OH)	Cl	2.60	44.0(63.6)	149.5(615.0)	-23.0	5.92(104),6.07(212)	128.3(35.6)
PhCH(OH)	Cl	2.71	47.8(61.0)	150.1(634.5)	- 5.7	5.83(96),5.94(215)	128.8(35.1)
PhCH=CHCH(OH)	Cl	2.58	45.5(61.0)	149.1(635.8)	-10.1	5.88(96),5.98(210)	129.1(33.1)
MeCH=CHCH(OH)	Cl	2.34	45.5(63.6)	149.7(653.1)	-21.2	5.85(99),5.94(212)	128.3(35.3)
Me	Me	2.17[a]	33.6(48.3)	157.3(452.7)	[a]	5.10(76),5.65(164)	123.2(35.6)
Me$_3$Si	Me	1.81	30.5(52.1)	151.9(455.2)	-34.9[b]	5.00(78),5.42(164)	123.3(35.6)
Me$_3$Ge	Me	1.95	30.2(53.4)	152.5(455.2)	-35.9	5.00(74),5.43(162)	122.6(36.9)
Me$_3$Pb	Me	2.67	30.7(58.5)	145.8(450.1)	-36.6[c]	4.78(80),5.40(158)	119.7(38.1)
Me$_2$C(OH)	Me	2.42	53.9(40.7)	152.5(456.5)	-35.7	5.32(78),5.70(158)	128.7(34.3)
PhC(Me)OH	Me	1.83	54.4(40.7)	152.0(462.8)	-34.4	5.30(76),5.67(156)	129.7(33.1)
MeCH(OH)	Me	2.42	50.6(43.2)	152.4(441.2)	-33.7	5.18(72),5.67(156)	128.0(33.1)
EtCH(OH)	Me	1.93	48.4(42.0)	152.7(436.1)	-34.0	5.28(74),5.73(152)	128.3(33.1)
PhCH(OH)	Me	2.16	50.6(43.2)	152.1(441.2)	-34.1	5.30(76),5.70(152)	128.2(30.5)
CH$_2$CH=CH$_2$	Me	2.32	40.2(47.1)	154.8(447.6)	-35.1	5.10(72),5.68(160)	124.8(33.1)
PhCH$_2$	Me	2.60	42.6(48.3)	154.7(445.0)	-34.3	5.15(72),5.67(156)	125.8(34.3)
PhCH=CHCH$_2$	Me	2.38	40.5(45.7)	154.7(445.0)	-34.8	5.10([a]),5.67([a])	125.0(35.6)
MeCH=CHCH$_2$	Me	1.97	41.0(45.8)	154.9(451.4)	-35.8	5.13(76),5.62(156)	124.7(35.6)
HC≡CCH$_2$	Me	2.42	39.1(48.3)	153.2 ([a])	-33.4	5.13([a]),5.75([a])	125.6(31.8)

Values in parentheses are those for ^{n}J(Sn,H) and ^{n}J(Sn,C).

[a] not determined; [b] ^{2}J(Sn,Si) 11.3 Hz; [c] ^{2}J(Sn,Pb) 1339.2 Hz.

Attempted palladium-catalysed coupling using (II)

(II) (5.6 g, 15 mmol), allyl, benzyl, crotyl or cinnamyl bromide or allyl acetate (15 mmol) and PhCH$_2$PdCl(PPh$_3$)$_2$ (1.5 mmol) were heated at 75°C; glyme (15 mL) was added to the reaction mixtures containing benzyl and cinnamyl bromide . Reaction times were 17 h, 8 d, 1 d and 2 d respectively. In the cases of allyl and cinnamyl bromides distillation at 14 mm Hg yielded a mixture of trimethyltin bromide and allyl or crotyltrimethyltin; in the other cases separation was possible; benzyltrimethyltin was obtained in 84% yield and cinnamyltrimethyltin in 57% yield. Trimethyltin acetate precipitated out from the reaction mixture when allyl acetate was used, and allyltrimethyltin was obtained in 68% yield.

In the absence of the catalyst, allyl bromide reacted only to the extent of ca. 5% after heating for 2.5 d. In the absence of allylic derivatives (II) decomposed to the extent of 35% after 2.5 d to give hexamethylditin and (presumably) allene. No reaction was observed under the same conditions when $RhCl(PPh_3)_3$ was used as a catalyst.

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