A New Synthesis of Vinyltins by Reaction of Phosphorus Ylides with Acyltins

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Acyltins react with various phosphorus ylides to afford the corresponding vinyltin derivatives, an alternative methodology for the preparation of these useful reagents. This method has been applied to the synthesis of functionally substituted vinyltins.

Recently, acyltin reactions, *e.g.* palladium-catalysed cross-coupling with acyl chlorides to afford diketones in reasonable yields, have shown the potential of these reagents as acyl anion precursors.[1,2] However, the instability of the reagents and their poor results with other coupling partners have led to masked acyltins being advantageously employed.[3–5] Enantioselective reduction of acyltins has also been used to prepare chiral α-alkoxy tin compounds.[6–8]

In connection with our interest in the synthetic potential of these organometallic reagents, we report herein the synthesis of vinyltin compounds by reaction of acyltins with phosphorus ylides. Vinylorganotin reagents, important intermediates for organic synthesis,[9] are most conveniently prepared by the addition of trialkyltin hydrides or stannyl anions to acetylenic compounds.[10–12] These reactions, however, are often poorly regioselective, except in the case of the hydrostannation of triple bonds substituted by strongly electron-withdrawing groups (CO_2R and C≡N *etc.*) which affords mainly, or even exclusively, the α-adducts. Since the reactions of ketones and aldehydes with phosphorus ylides produce alkenes with unambiguous positioning of the double bond,[13,14] a similar methodology using acyltins would provide an alternative way for the preparation of defined vinyltins.

Two basic types of reaction have been performed: the reactions with phosphoranes and the reactions with phosphonate anions. The results for typical reactions with phosphoranes (prepared by treating phosphonium salts with BuLi) are shown in Table 1.

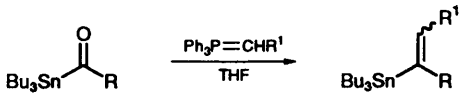


Table 1 Reaction of phosphoranes with acyltins[a]

Entry	R	R^1	Product	Yield[b]
1	Me	H	$Bu_3SnC(Me)=CH_2$	52
2	Et	H	$Bu_3SnC(Et)=CH_2$	53
3	Pr^i	H	$Bu_3SnC(Pr^i)=CH_2$	54
4	Et	Me	(*Z*)-$Bu_3SnC(Et)=CHMe$	30
5	Et	Et	—	—

[a] The reaction failed in ether. [b] Isolated yield %.

These results show that the reaction is sensitive to steric hindrance, the ethylidene ylide giving only a poor yield of the desired product (entry 4) and the propylidene ylide failing to give any (entry 5).

For the preparation of β-substituted vinyltins bearing electron-withdrawing groups, the corresponding phosphonates were used since they offer several advantages: they allow condensations with relatively unreactive carbonyl compounds and the water-soluble phosphate residues are easily eliminated.[15,16] The phosphonate anions (obtained by adding the phosphonate at room temperature to a suspension of sodium hydride in diglyme) react with acyltins as shown in Table 2.

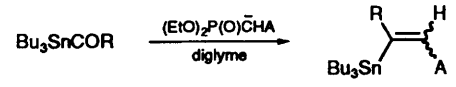


Table 2 Reaction of phosphonates with acyltins

Entry	R	A	*Z*/*E*[a]	Yield[b]
1	Me	CN	28/72	70
2	Et	CN	25/75	70
3	Pr^i	CN	40/60	62
4	Me	CO_2Me	80/20	40
5	Et	CO_2Me	60/40	37
6	Pr^i	CO_2Me	57/43	27

[a] *Z*/*E* ratios were determined by GC. [b] Isolated yield %.

It can be seen that ester-containing vinyltins have been obtained in low yields, which were improved by employing cyclic phosphonates: these reagents react *ca.* 20 times faster than their acyclic counterparts[17] (Table 3).

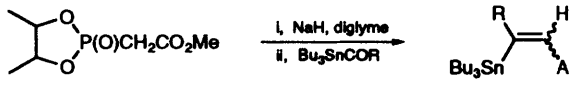
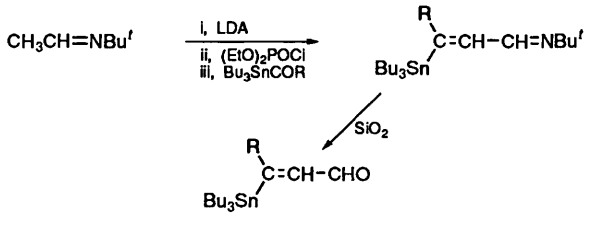


Table 3 Reaction of a cyclic phosphonate with acyltins

Entry	R	*Z*/*E*	Yield (%)
1	Me	33/67	60
2	Et	37/63	67
3	Pr^i	45/55	58

Because of the wide choice of phosphorus reagents, this method has considerable interest for the preparation of substituted vinyltins, almost inaccessible by other ways. For example, an α,β-unsaturated β-stannyl imine and the corresponding aldehyde were easily prepared using diethyl chlorophosphate and *N*-ethylidene-*tert*-butylamine (Table 4).

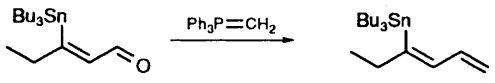


The metallation of *N*-ethylidene-*tert*-butylamine with an excess of lithium diisopropylamide, followed by introduction of diethyl chlorophosphate and addition of acyltins, affords α,β-unsaturated β-stannyl imines which, after a simple filtration through silica gel, provide the corresponding aldehydes in satisfactory yields. These new organotin derivatives are very versatile synthons, which can, for example, be homologated by a Wittig reaction to provide 4-tributylstannylhexa-1,3-diene in 50% yield.

Table 4 Preparation of α,β-unsaturated β-stannylimine and aldehyde

	Imine		Aldehyde	
R	Yield[a]	Z/E[c]	Yield[b]	Z/E[c]
Et	70	81/19	90	83/17
Pr^i	70	95/5	88	96/4

[a] Isolated yield (%). [b] Isolated yield (%) based on the stannic imine. [c] Z/E ratio.



Experimental

The diethyl phosphonates were prepared by an Arbuzov reaction using triethyl phosphite and alkyl halides.[18] The cyclic phosphonate was obtained according to a literature procedure.[19,20]

General Procedure for the Reaction of Phosphoranes: Synthesis of 2-Tributylstannylpropene.—To a stirred solution of methyl(triphenyl)phosphonium iodide (5.5 mmol) in THF (30 cm^3) at 0 °C, BuLi (2.5 mol dm^{-3} in hexane; 2.1 cm^3, 5.25 mmol) was added under nitrogen. The mixture was stirred at room temperature for 1 h and recooled to 0 °C. Acetyltributylin (5 mmol) was then added to the red solution and the mixture was stirred overnight at room temperature; it was then treated with a saturated aqueous NH_4Cl and extracted with light petroleum. The extract was dried ($MgSO_4$) and evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (elution with pentane); δ_H(250 MHz, $CDCl_3$) 0.6–1.8 (m, 27 H), 2.01 (br s, 3 H), 5.22 (br s, 1 H, J_{SnH} 58) and 5.7 (br s, 1 H, J_{SnH} 136); δ_{Sn}(74.5 MHz, C_6D_6) − 44.98; *m/z* 275 (88), 219 (100), 163 (80) and 121 (34).

General Procedure for the Reaction of Phosphonates: Preparation of (E)- *and* (Z)-*Methyl* 3-*tributylstannylbut*-2-*enoate.*—The phosphonate (5 mmol) dissolved in solvent (3 cm^3) was added to a stirred slurry of sodium hydride (5 mmol) in diglyme (30 cm^3) at room temperature under nitrogen. After the mixture had been stirred at room temperature for 1 h, gas evolution had ceased. To this mixture, acetyltributyltin (5 mmol) was added and the mixture stirred overnight at 120 °C. An excess of water was added to the cooled mixture and the product extracted with ether. The extract was dried ($MgSO_4$) and concentrated under reduced pressure and the crude product was was purified by column chromatography; δ_H(250 MHz, $CDCl_3$) (*Z* isomer) 0.6–1.5 (m, 27 H), 2.10 (br s, 3 H), 3.65 (s, 3 H), 6.32 (br s, 1 H, J_{SnH} 106); (*E* isomer) 0.6–1.6 (m, 27 H), 2.3 (br s, 3 H), 3.55 (s, 3 H) and 5.8 (br s, 1 H, J_{SnH} 64); δ_{Sn}(74.5 MHz, C_6D_6) −50.6 (*Z* isomer) and −33.4 (*E* isomer).

Formylolefination.—To a cooled solution (−78 °C) of LDA [from BuLi (30 mmol) and diisopropylamine (30 mmol) in THF (80 cm^3)], was added *N*-ethylidene-*tert*-butylamine (15 mmol) and the mixture was stirred for 30 min. Diethyl chlorophosphate (15 mmol) was added to it at −78 °C and the whole stirred for 2 h while being allowed to warm to −10 °C; it was then recooled to −78 °C. Propionoyltributyltin (10 mmol) was added to the mixture which was then stirred for 30 min at −78 °C and allowed to warm to room temperature overnight. The mixture was treated with saturated aqueous NH_4Cl and the aqueous layer separated and extracted with light petroleum. The extract was dried and concentrated and the residue distilled *in vacuo* to give the α,β-unsaturated imine; b.p. 135–140 °C at 0.1 mmHg; δ_H(250 MHz, $CDCl_3$) (*Z* isomer) 0.6–1.5 (m, 30 H), 1.05 (s, 9 H), 2.3 (q, 2 H, *J* 7, J_{SnH} 44), 6.7 (d, 1 H, *J* 8.7, J_{SnH} 121), 7.8 (d, 1 H, *J* 8.7); (*E* isomer) 0.6–1.5 (m, 39 H), 2.6 (q, 2 H, *J* 7), 6.23 (d, 1 H, *J* 8.7, J_{SnH} 63), 8.23 (d, 1 H, *J* 8.7); δ_{Sn}(74.5 MHz, C_6D_6) −49.9 (*Z* isomer) and −37.2 (*E* isomer).

The corresponding aldehyde was obtained simply by passing the imine in light petroleum through a silica gel column; δ_H(250 MHz, $CDCl_3$) (*Z* isomer) 0.6–1.5 (m, 30 H), 2.5 (q, 2 H, 7, J_{SnH} 43.5), 6.6 (dt, 1 H, *J* 1.4, 6.3, J_{SnH} 105), 9.45 (dt, 1 H, *J* 1.5, 6.3); (*E* isomer) 0.6–1.5 (m, 30 H), 2.8 (m, 2 H), 6.1 (br d, 1 H, 7.9, J_{SnH} 62), 9.95 (dt, 1 H, *J* 1.6, 7.9); δ_{Sn}(74.5 MHz, C_6D_6) −45 (*Z* isomer), −34.89 (*E* isomer) (Found: C, 54.7; H, 9.25. Calc. for $C_{17}H_{34}OSn$: C, 54.72; H, 9.18%).

This aldehyde reacted with methylenephosphorane as described for the acyltin derivatives to give the expected diene in 50% yield after column chromatography on silica gel with pentane as eluent: δ_H(250 MHz, $CDCl_3$) (*Z* isomer) 0.6–1.7 (m, 30 H), 2.2 (q, 2 H, *J* 7.4), 4.95 (dd, 1 H, *J* 1.7, 10), 5.03 (dd, 1 H, *J* 1.7, 18.9), 6.2 (m, 1 H, *J* 18.9, 10, 10.6), 6.6 (d, 1 H, *J* 10.6 Hz, J_{SnH} 125); δ_C(62.9 MHz, $CDCl_3$) 10.52 (CH_2), 13.02 (CH_3), 14.25 (CH_3), 27.1 (CH_2), 29.2 (CH_2), 33.96 (CH_2), 116.14 (=CH_2), 136.59 (CH=), 138.24 (CH=) and 153.85 (C=); δ_{Sn}(74.5 MHz, C_6D_6) −49.28 (*Z* isomer) and −42.35 (*E* isomer).

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