Monoalkylstannanes as a New Source of Allyl Radical Transfer

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The straightforward preparation of monoallylstannanes **2**, which are very useful in allylic radical transfer, provides a readily available source of functionalized allyl synthons; a 'one-pot' procedure associated with a simple work-up represents a significant step in the use of allyltins in radical reactions.

Allyl radical transfer mediated by allyltributyltin was discovered more than twenty years ago[1] and developed by Keck.[2] It has since been successfully applied to the total synthesis of various natural compounds[3] and represents one of the most interesting methods for introducing allyl groups under mild and neutral conditions. Nevertheless, this radical chain methodology suffers from two serious drawbacks. The first lies in the difficulties often encountered for synthesizing functionalized allylic tin substrates despite the advances made by Baldwin.[4] Secondly, the use of allyltrialkyltins produces toxic triorganotin by-products which in general cannot be easily removed from the reaction products.

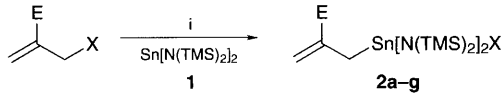
In the course of our studies of the synthesis of new monoallyltins, we were interested in the stable stannylene **1** isolated by Lappert and Zuckerman,[5] and decided to check its reactivity with various allyl halides. Surprisingly, considering its ready availability, this monomeric stannous reagent has hardly been used for synthetic purposes.[6] We found its insertion to be general for a wide range of allylic substrates (Scheme 1), under particularly mild conditions.† Furthermore, all the monoallylstannanes **2a–g** (Table 1) were obtained simply after evaporation of the solvent, in quantitative yields and appeared to be stable when protected from moisture.‡

We were then interested in studying their ability for transfering the allylic moiety under radical conditions (Scheme 2), similar to those usually chosen with allyltributyltin reagents.§ Previous attempts have been made in this area, with monoallyltrihalogenotins,[7] which led almost exclusively to the dimerization product of the allylic group due to a competitive abstraction of the halogen on the organotin reagent by the $X_3Sn^{\cdot}$ radical. In contrast, the experiments made with **2g** gave the desired allylic transfer product **3a–d** in fairly good yields (Table 2). We thus established the fact that, unlike trihalogenotin radicals, the $[N(TMS)_2]_2BrSn^{\cdot}$ radical is efficient and selective enough towards halogen abstraction to authorize a good radical chain turn-over.

To the best of our knowledge, this is the first time that monoalkyltins have been used for the radical transfer of an organic moiety. Moreover, the organotin side product $SnBr_2[N(TMS)_2]_2$ remains particularly sensitive towards hydrolysis leading to a non-toxic 'inorganic' tin residue, allowing easy purification of the products **3** from all tin residues, simply by flash chromatography on silica gel.

Finally, as the synthesis of the precursors **2a–g** were possible in various solvents (*i.e.* hydrocarbons, aromatics and ethers) without any noticeable change in the reactivity of the stannylene **1**, it seems interesting to check if a one-pot procedure could be applied (Scheme 3). As expected, the products of the allylic radical transfer **3d–e** were isolated in similar yields compared to the two step procedure.

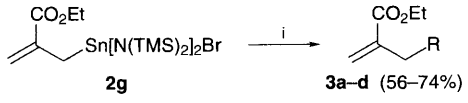
This new methodology, taking advantage of the straightforward production of the monoallyltins **2**, coupled with their reactivity and the ease of purification of the reaction products **3**,



Scheme 1 *Reagents and conditions*: i, **1** (1 equiv.), diethyl ether or benzene, room temp.

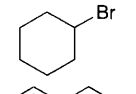
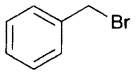
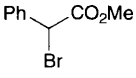
Table 1 Preparation of monoallyltins reagents

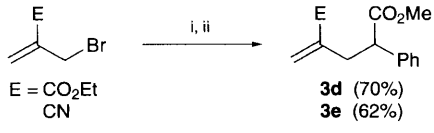
Product	E	X	*T*/h	δ (^{119}Sn NMR)
2a	H	Cl	48	−51.2
b	H	Br	0.2	−84.1
c	Cl	Cl	48	−66.8
d	Cl	I	0.2	−194.0
e	Ph	Br	0.2	−92.8
f	CN	Br	0.2	−99.5
g	CO_2Et	Br	0.2	−129.6



Scheme 2 *Reagents and conditions*: i, Alkyl halide RBr (0.85 equiv.), AIBN (cat.), benzene, reflux

Table 2 Allylic radical substitution on bromoalkanes

Allylstannane	Alkyl halide	Product (Yield %)¶
2g	$C_{10}H_{21}Br$	**3a** (56)
2g		**3b** (71)
2g		**3c** (73)
2g		**3d** (74)



Scheme 3 *Reagents and conditions*: i, **1** (1 equiv.), benzene, room temp., ii, $PhCHBrCO_2Me$ (0.83 equiv.), AIBN (cat.), reflux

considerably broadens the scope of the allyl radical transfer with organotin reagents.

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Footnotes

† All new compounds were characterized by IR, ^{1}H, ^{13}C and ^{119}Sn NMR, mass spectroscopy and accurate masses. *Selected spectroscopic data* for **2g**; IR (film)/cm^{-1}: 2985, 2956, 2899, 1661, 1613, 1336, 1249, 1202, 898, 867, 840, 760 and 678; ^{1}H NMR ($CDCl_3$, 250 MHz) (*J* values in Hz) δ 6.18 (bs, 1 H, J_{HSn} 20.9), 5.69 (bs, 1 H, $^4J_{HSn}$ 34.6), 4.25 (q, 2 H, *J* 7.2,), 2.64 (bs, 2 H, $^2J_{HSn}$ 98.5), 1.31 (t, 3 H, *J* 7.2,) and 0.22 (s, 36 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 169.3 ($^3J_{CSn}$ 29), 135.3 ($^2J_{CSn}$ 76), 125.3 ($^3J_{CSn}$ 97), 62.3, 34.4 ($^1J_{CSn}$ 650), 14.2 and 5.8; *m/z*: 632 ($M^{+\cdot}$), 617 ($M^{+\cdot}$-CH_3), 553 ($M^{+\cdot}$-Br). Acc. mass (for $C_{17}H_{41}N_2O_2BrSi_4Sn$): calc. 617.0529, obtained 617.0549.

‡ There is no exchange reaction between bistrimethylsilylamino and halogeno ligands, contrary to when allyltrihalogenotins ligands are used.[7,8] This implies that the Sn–N bond is much stronger than a tin–halogen or a normal tin–nitrogen bond.

§ It is noteworthy that all the radical reactions were conducted with a smaller excess of tin reagent (1.2 equiv.) and more dilute conditions (0.2 mol dm^{-3}) compared to those typically used (2.0 equiv. and 0.5 mol dm^{-3}) with allyltributyltin reagents.

¶ Yields reported were calculated after purification of the products **3** by silica gel column chromatography. Typical one-pot procedure: Bis(*N,N*-bistrimethylsilylamino)stannylene **1** (1.00 g, 2.27 mmol) and ethyl 2-(bromomethyl)but-2-enoate (439 mg, 2.27 mmol) were mixed in anhydrous benzene (10 ml) under an inert atmosphere. After stirring for 30 min. at 25 °C, methyl 2-bromo-2-phenylethanoate (432 mg, 1.89 mmol) and catalytic amounts of AIBN were added and the solution was heated to reflux for 8 h. The reaction mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (light petroleum–diethylether 9 : 1), providing **3d** as a colourless oil (347 mg, 70%).

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