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Preliminary Communication

A convenient synthesis of functionalized allyltrihalostannanes

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Abstract

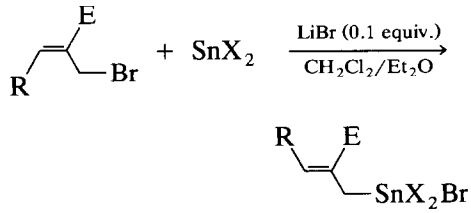
Functionalized monoallyltin halides can be prepared readily in excellent yields by the direct reaction of stannous halides with allyl bromides in the presence of lithium bromide as catalyst. Non-coordinating solvents are necessary, and the reaction involves a double S_N2' substitution.

1. Introduction

Despite the dramatic surge in the applications of organotin compounds in organic synthesis, alkyltin trihalides have received little attention from synthetic chemists although they were discovered more than one hundred years ago [1]. The main limiting factor has been the lack of a convenient method for their preparation that does not also give by-products such as di- or tri-alkyltin halides [2]. Further difficulties lie in the high reactivity of the Sn–X bond, which promotes premature reactions of the products.

Two approaches leading to trichlorostannyl ketones have been developed in the last fifteen years. The first involved the addition of trichlorostannane, generated *in situ*, to α,β-unsaturated ketones [3]. The second used the reaction of tin tetrachloride with ketones, silyl enol ethers, [4] or siloxycyclopropanes [5,6]. The syntheses of trichlorostannyl esters were also achieved by these routes [2,7]. The preparation of allylbromodichlorotin was reported by Tagliavini [8], but this method is still limited to the unsubstituted allyl group.

In this paper, we report an original procedure for the synthesis of functionalized allyltrihalogenostannanes by direct reaction of stannous halides and substituted allyl bromide in the presence of catalytic amount of lithium bromide.



(R = H, Me; E = COOEt, COMe; X = Cl, Br)

2. Experimental details

As a typical procedure, we describe the reaction between ethyl 2-(bromomethyl)but-2-enoate **2** and stannous chloride.

In a 50 ml three-neck round-bottom flask were mixed the (*Z*)-allylic bromide **2** (2.17 g, 10.5 mmol) and stannous chloride (2.00 g, 10.5 mmol) under an inert atmosphere. After addition of dichloromethane (4 ml), anhydrous ether (4 ml), and lithium bromide (90 mg, 1.0 mmol), the mixture was heated at reflux for 1 h. After cooling and concentration under reduced pressure, the residue was dissolved in chloroform (20 ml) and filtered. Removal of the solvent gave the crude monoallylstannane **7** as a yellow oil (3.98 g, 96%) which could be used without any further purification. However, the product was purified by Kugelrohr distillation (135°C/10^{-4} mmHg) with a minimum of decomposition, providing (*E*)-ethyl 2-(bromodichlorostannylmethyl)but-2-enoate (**7**) as a pale yellow liquid (3.49 g, 84%).

Spectral data for **7**: ^{1}H NMR (250 MHz in $CDCl_3$) δ (ppm) *J* (Hz): 7.31 (1H, qt, *7.1, 2.1*), 4.45 (2H, q, *7.1*), 2.83 (2H, s, $^2J(^1H-^{119}Sn)$ *117.6*), 2.05 (3H, dt, 7.1, 1.4, $^5J(^1H-^{119}Sn)$ *25.2*), 1.41 (3H, t, *7.1*). ^{13}C NMR (63 MHz in $CDCl_3$) δ (ppm) *J* (Hz): 173.6 (C=O), 144.9 (=CH, $^3J(^{13}C-^{119}Sn)$ *152*), 123.8 (=C<, $^2J(^{13}C-Sn)$ *68*), 65.5 (O–CH_2), 27.1 (CH_2–Sn, $^1J(^{13}C-^{119}Sn)$ *837*), 16.7 (CH_3–CH), 14.1 (CH_3–CH_2). ^{119}Sn NMR (75 MHz in $CDCl_3$) δ (ppm): −154.7 (R–$SnCl_3$), −219.1

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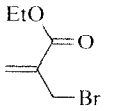
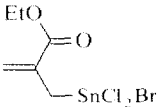
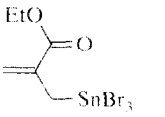
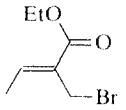
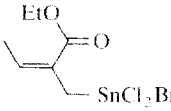
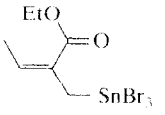
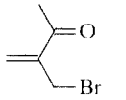
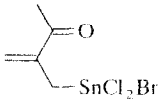
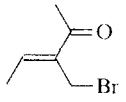
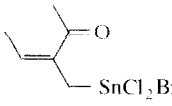
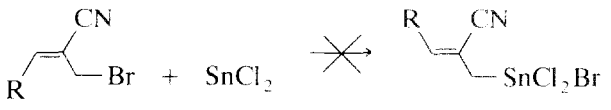
TABLE 1. Synthesis of monoallyltrihalostannanes starting from allyl bromides and stannous halides

Substrate	Tin halide	Allyltrihalostannane		Yield % [10*]
 1	$SnCl_2$		5	74
	$SnBr_2$		6	61
 2	$SnCl_2$		7	84
	$SnBr_2$		8	85
 3	$SnCl_2$		9	87
 4	$SnCl_2$		10	94

(R–$SnCl_2Br$), −284.8 (R–$SnClBr_2$), −350.9 (R–$SnBr_3$) [9*]. IR (film) ν (cm^{-1}): 1635 (C=C), 1605 (C=O), 1310 (C–O). Other results are summarized in Table 1.

3. Results and discussion

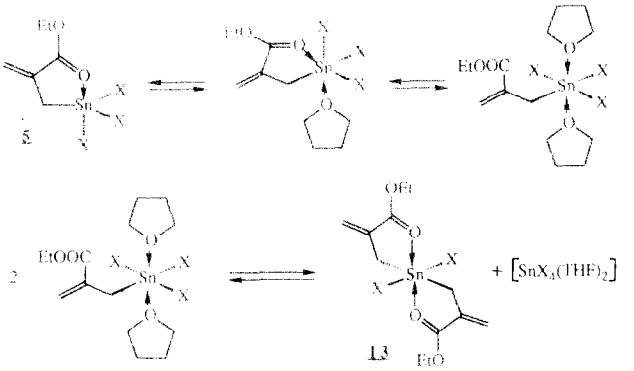
Allyltin halides **5** to **10** are stable at room temperature in the absence of moisture. Intramolecular complexation of the tin atom by the carbonyl group plays an important role in the stability of the product and possibly in the mechanism of the reaction itself. Indeed, we have never been able to prepare **12** corresponding to the reaction of the halide **11** with stannous chloride under these conditions.



11 (R = Me, ^{i}Pr or Ph) **12**

The intramolecular Sn–O coordination was clearly shown in the IR spectra by the substantial shift of the C=O band (1605 cm^{-1} for **7**). It is known that the intramolecular chelation can be broken by coordinating solvents [11], leading to a hexacoordinate tin atom. This controls the choice of the solvent, which is essential for the selectivity of the reaction. In order to obtain only monoallyltin compounds, weakly coordinating conditions are necessary, whereas tetrahydrofuran led to a mixture of mono- and di-allyltin compounds in the ratio of 2.3 : 1.

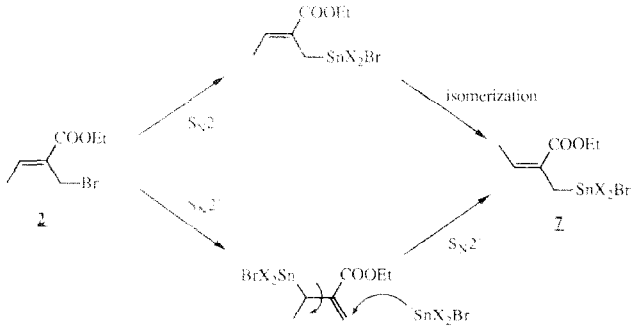
The diallyltin product probably comes from a redistribution reaction between two monoallyltin halides complexed by tetrahydrofuran, leading to stannic halide and hexacoordinate diallyldihalogenostannane **13**.



Allyltin halides are obtained with or without lithium bromide, but a catalytic amount of it increases the rate of the reaction over one hundred fold. Hence, the reactive species must be the nucleophile BrX_2Sn^- in this case [12].

Moreover, the stereochemistry at the double bond in product **7**, based on the coupling constant values, showed that isomerisation occurred during the reaction. Allyl bromides **2** and **4** show (*Z*) stereochemistry [13], whereas the coupling constants observed for **7** were consistent with an (*E*) stereochemistry. A NOESY experiment on **10** showing a correlation between the two methyl groups proved their spatial closeness, confirming isomerization about the olefinic bond.

The stereochemistry of **7** cannot be explained by an S_N2 type mechanism, nor does the structure fit with S_N2' substitution. It is necessary to invoke mechanisms involving two successive steps.



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

The reaction pathway requiring double allylic substitution seems to be the most probable, since previous studies in our laboratory led to isolated intermediates resulting from preliminary S_N2' attack of various nucleophiles, such as tert-butylperoxylates [14] or sulfinates [15] on the allyl bromide **2**.

In summary, the synthesis described above provides an easy and direct way to substituted monoallylstannanes. This novel method holds considerable synthetic promise starting either from allyltin halides themselves [6,16] or from alkylated derivatives [17]. Further studies in this field are now in progress.

References and notes

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9 As a result of rapid halogen exchange, the products **5**, **7**, **9** and **10** were, in fact, a mixture of the four species $RSnCl_3$, $RSnCl_2Br$, $RSnClBr_2$, $RSnBr_3$. The proportions (%) were close to the statistical values (30:44:22:4). These isomers were easily distinguished by ^{119}Sn NMR spectrometry and by mass. On the other hand, ^1H and ^{13}C NMR spectroscopy generally gave average values.

10 Yields are those obtained after distillation (**5**, **6**, **7**, **8**) or crystallisation (**9**, **10**). Due to the thermal sensitivity of the products, yields of the crude products are slightly higher, and the allyltin trihalides can be used without any purification.

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