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1,1-Bis(Trialkylstannyl)ethenes: Further Investigations into their Reactivity

Peter Quayle*, Jingyang Wang and Jie Xu

Department of Chemistry

The Victoria University of Manchester

Manchester M13 9PL, UK.

E-mail: Peter.Quayle@man.ac.uk

Christopher J. Urch

Zeneca Agrochemicals

Jealotts Hill Research Station

Berkshire.

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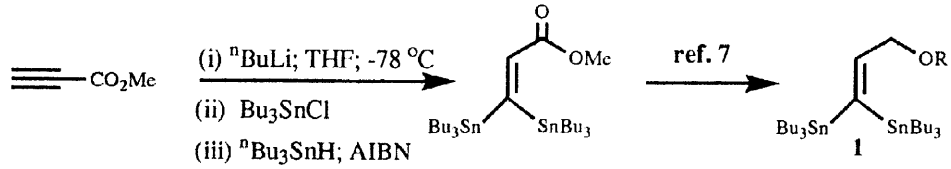
Abstract: *Ipso* halodestannylation of 1,1-*bis*(tributylstannyl)ethenes with one equivalent of halogen leads to a variety of 1-halovinylstannanes. In certain cases, these reactions exhibit high levels of stereoselectivity. A plausible mechanistic pathway is advanced in order to explain the stereochemical outcome of these reactions. Addition of two equivalents of halogen affords the corresponding 1,1-*bis*-haloalkenes complementing existing methodology (*e.g.* Corey-Fuchs reaction) for the preparation of these useful synthetic intermediates.

The chemistry of vinyl metallic species is the focus of much interest due to their almost universal application to the stereoselective synthesis of dienes, polyenes and ene-ynes in Stille-type coupling reactions[1]. In addition, vinyl silanes[2], stannanes[3] and boronic acids[4] undergo ipso-substitution reactions under mild conditions leading to a variety of functionalised olefins. Most attention has centred on the synthesis and reactivity of mono-metallic systems with only sporadic reports concerning the synthesis and functionalisation of bi-metallic reagents[5]. Recently we described[6] a route to *bis*-stannylethenes **1** and commented on their utility in the stereoselective synthesis of tri-substituted alkenes and allenes.[7] Subsequently[8] we have developed a more direct and robust route to **1** *via* the regioselective hydrostannylation of ethynylstannanes, **Scheme 1**.



Scheme 1

Further studies into the functionalisation of the stannanes **1** have involved investigations of their halodestannylation chemistry[9], providing access to halostannanes **2** which bear an equivalence to the hypothetical 1,1-dipoles. Initially the *bis*-stannylethenes **1a-1g** were treated with *ca.* 1 equivalent of iodine[10] in dichloromethane at 20 °C. In all cases a rapid reaction afforded the corresponding monoiodovinylstannanes as a

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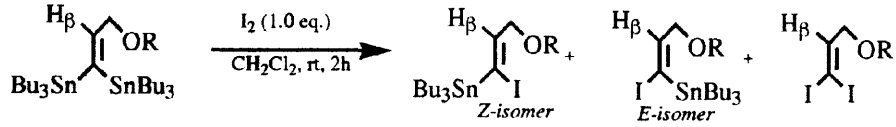
mixture of geometric isomers (2_Z and 2_E) in good isolated yields. In the case of **1a** and **1f** concomitant formation of the bis-iodoethenes **3a** and **3f** was observed. The stereochemical course of the reaction, **Table 1**, was readily elucidated from the magnitude of the vicinal coupling constant[11] between tin and H_β. Examination of **Table 1** reveals that the stereochemical outcome of these reactions is influenced by a modest steric component [*cf.* entries (1) and (5): *Z:E* ratio changes from 1.3:1 to 2:1]. A more pronounced effect is observed in the case of thiocarbamate **1c** (entry (3)), where the iodoalkenes $2c_Z$ and $2c_E$ were isolated in 81% overall yield, with a *Z:E* ratio of ≈10:1.



1 2_Z 2_E **3**

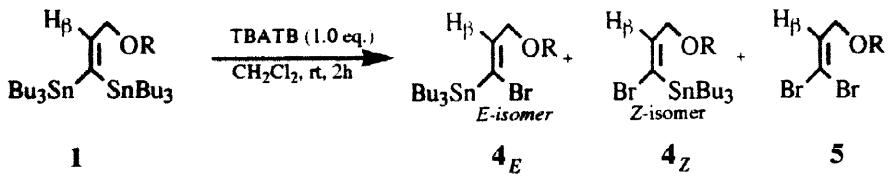
(Entry no.) Substrate no.[f]		Z-isomer; %	E-isomer; %	Yield[&] (%)
(1); R =H	**1a**	$2a_Z$ 46	$2a_E$ 36	61[@]
(2);R= CH_2OCH_3	**1b**	$2b_Z$ 55	$2b_E$ 45	91
(3); R= 	**1c**	$2c_Z$ 91	$2c_E$ 9	81
(4); R= 	**1d**	$2d_Z$ 62	$2d_E$ 38	55
(5); R= TBDMS	**1e**	$2e_Z$ 67	$2e_E$ 33	93
(6); R= $COCH_3$	**1f**	$2f_Z$ 59	$2f_E$ 24	72[$]
(7); R= COC_6H_5	**1g**	$2g_Z$ 67	$2g_E$ 33	90

[f] All new compounds were fully characterised by ir, ^{1}Hnmr, ^{13}Cnmr, mass spec. and/or combustion microanalysis. [&] Refers to purified yield after "flash chromatography". Isomeric iodostannanes are inseparable. [@] 13% yield of the di-iodide **3a** also isolated. [$] 15% yield of the di-iodide **3f** also isolated.

Table 1

Monobromodestannylation of the *bis*-stannylethenes **1** was also observed under mild reaction conditions using a number of reagents including Br_2-acetic acid and NBS.[12] From a practical standpoint, the stable crystalline perbromides are ideal reagents for this transformation: they are easy to handle and require no purification. Treatment of *bis*-stannnanes **1a-1e** and **1h** with tetra-*n*-butylammonium tribromide (TBATB) or pyridinium bromide perbromide (1.0 eq.) in dichloromethane at 20 °C, affords the corresponding monobromostannylethenes 4_E and 4_Z, in good isolated yields (*ca.* 70-80%), **Table 2**.

The reaction is compatible with a variety of functionality *e.g.* MOM ethers (entry (2)), thiocarbonyl groups (entry (3)) and olefinic centres (substrate **1h**, entry (6)). In comparison to the iododestannylation reaction, this reaction appears to be overall much less sensitive to steric effects [*cf.* **Table 2** entries (1) and (5); *Z:E* 1.7 to 1.4:1]. In the case of thiocarbamate **1c** the reaction proceeded with a stereochemical outcome (*E:Z* ≈ 6:1) opposite to that anticipated on the basis of simple steric arguments [*cf.* **Table 2**, entry (5)].



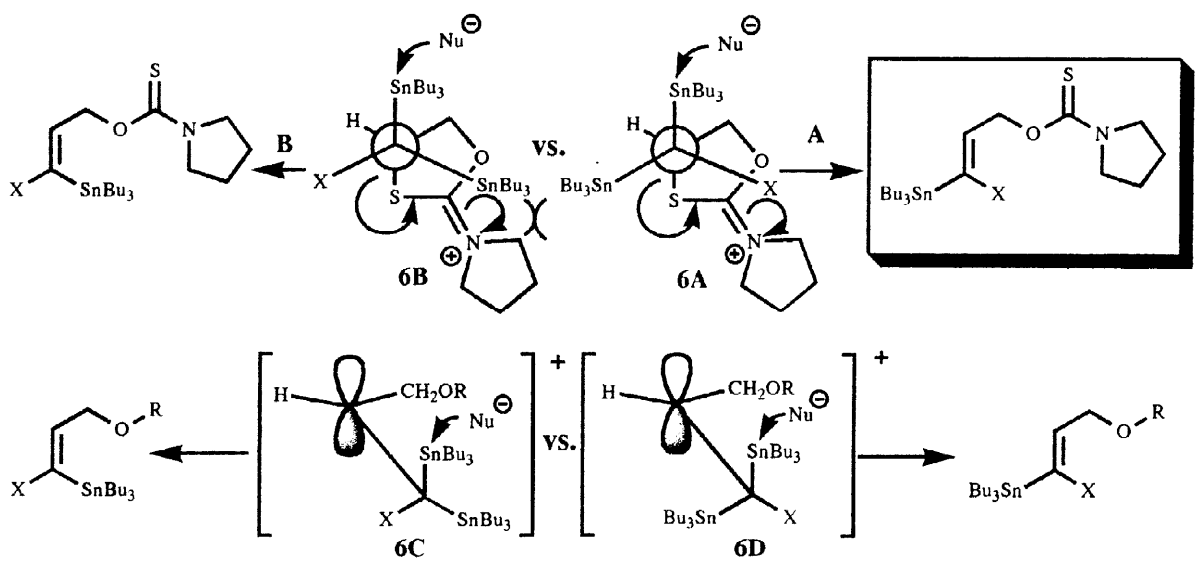
1 4_E 4_Z 5

(Entry no.) Substrate no.[£]		*E*-Isomer ; %	*Z*-Isomer; %	Yield[&] (%)
(1); R= H	**1a**	$4a_E$ 33	$4a_Z$ 56	82[@]
(2); R= CH_2OCH_3	**1b**	$4b_E$ 33	$4b_Z$ 67	81
(3); R= 	**1c**	$4c_E$ 86	$4c_Z$ 14	59
(4); R= 	**1d**	$4d_E$ 43	$4d_Z$ 57	96
(5); R= TBDMS	**1e**	$4e_E$ 42	$4e_Z$ 58	89
(6); R= $CH_2(CH)_2C_6H_5$	**1h**	$4h_E$ 33	$4h_Z$ 67	73

[£]All new compounds were fully characterised by ir, ^{1}Hnmr, ^{13}Cnmr, mass spec. and/or combustion microanalysis. [&]Refers to purified yield after "flash chromatography". Isomeric bromostannanes are inseparable. [@] 10% yield of the di-bromide **5a** also isolated.

Table 2

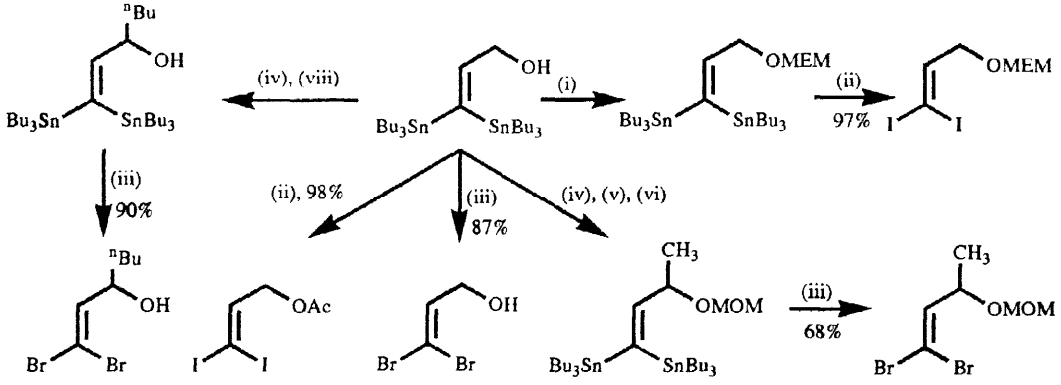
A plausible explanation for these observations invokes the formation of a cyclic intermediate **6** in reactions of thiocarbamate **1c** with positive halogen sources.[13] Assuming that collapse of **6** takes place in an *antiperiplanar* sense,[14] then pathway **6A** would be preferred on steric grounds to pathway **6B**.



Scheme 2

In the case of substrates possessing less polarizable substituents, such as ether **1b**, amide **1d** and ester **1f**, reaction with positive halogen sources would be most likely to proceed *via* transition states **6C** or **6D**, leading to products with diminished levels of stereoselection, **Scheme 2**.

Finally, exposure of a range of *bis*-stannylethenes to two equivalents of TBATB, or iodine in CH_2Cl_2, at ambient temperature, results in their clean conversion to the corresponding dibromo- or di-iodoethenes, **Scheme 3**. 1,1-Dihaloalkenes are valuable intermediates[15] in their own right and this methodology nicely complements existing methods for their preparation, most notably the Corey-Fuchs reaction.[16]



Reagents and conditions: (i) ref.7; (ii) I_2, 2 eq.; CH_2Cl_2; 20 °C; (iii) TBABT, 2 eq.; CH_2Cl_2; 20 °C; (iv) TPAP, 6 mol%; NMO, 2 eq.; CH_2Cl_2; 4Å sieves; 20 °C; 78 %; (v) MeLi, 1 eq.; THF; -78 °C; 84%; (vi) MOM-Cl, 1 eq.; Hünig's base, 1.2 eq.; CH_2Cl_2; 20 °C; 77%; (vii) Ac_2O, 1.2 eq.; pyridine; DMAP, 1 eq.; Et_2O; 95% (viii) ^{n}BuLi, 1 eq., THF, -78 °C; 74%.

Scheme 3

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