

## Unexpected Temperature-dependent Stereoselectivity in the Thermolysis of 2-Trialkylstannyl Alcohols

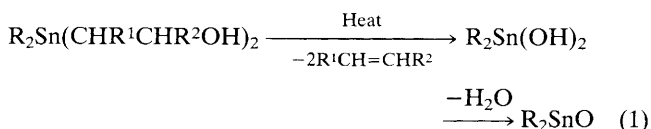
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Thermolysis of substituted 2-trialkylstannyl alcohols reveals a complete reversal of selectivity between 100 and 160 °C *i.e.* an *erythro* 2-trialkylstannyl alcohol leads to an (*E*)-alkene at 100 °C or a (*Z*)-alkene at 160 °C; this unexpected result depends on the formation of trialkyltin alkoxide intermediates and allows the preparation of isomeric alkenes from the same precursor by simply changing the reaction temperature.

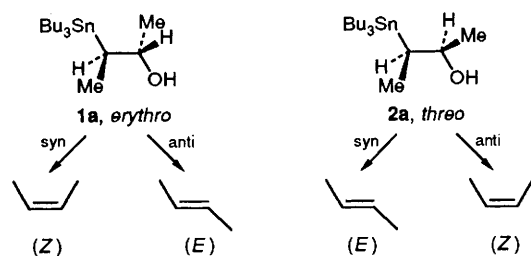
We have recently shown that the thermal decomposition of bis(2-acyloxyalkyl)dialkylstannanes gives dialkyltin dicarboxylates. This property allows the use of these organotin compounds as latent catalysts for silicone curing and polyurethane preparation: when heated, they liberate the active species *in situ* and the mixtures in which they have been incorporated are rapidly cured or polymerized.<sup>1</sup> The corresponding alcohols, bis(2-hydroxyalkyl)dialkyltins can undergo such a decomposition to give formally dihydroxydialkyltins, which dehydrate to dialkyltin oxides,<sup>2</sup> efficient catalysts for the above mentioned applications,<sup>3</sup> [eqn. (1)]. Therefore, these alcohols are good candidates as latent catalysts.



To elucidate the decomposition mechanism of these 2-organostannyl alcohols and to investigate the possible influence of substituents on the hydroxylated carbon chain a stereochemical study was undertaken.  $\beta$ -Elimination in 2-metallated alcohols is a well documented reaction in organosilicon chemistry where the Peterson alkenation has multiple synthetic applications.<sup>4,5</sup> In organotin chemistry as well, this process proves to be an efficient route to various

alkenes.<sup>6</sup> Previous studies have shown that an *anti* elimination involves an open chain transition state and that it can be accelerated by electron-donating substituents on the hydroxy bearing carbon atom. A *syn* elimination corresponds to a closed transition state and is accelerated by electron-withdrawing substituents on the metallated carbon atom.<sup>4,7</sup> The required substituted 2-tributylstannyl alcohols have been obtained by the stereospecific opening of (*E*)- or (*Z*)-but-2-ene oxide with lithium tributyltin.<sup>8,9</sup> This very clean reaction affords respectively *erythro*-3-tributylstannylbutan-2-ol **1a** or *threo*-3-tributylstannylbutan-2-ol **2a** as racemic mixtures in good yield and high purity. Thermolysis<sup>†</sup> of the *erythro* alcohol **1a** at 100 °C for 6 h furnishes a mixture of butenes, the major component being (*E*)-but-2-ene. Under the same conditions, the *threo* alcohol **2a** gives mainly (*Z*)-but-2-ene. These decompositions are thus stereoselective and result from an *anti* elimination as it has been reported for the acid catalysed elimination in 2-trialkylsilyl or 2-trialkylstannyl alcohols.<sup>4,7</sup> When the thermolysis of **1a** or **2a** is carried out at higher temperature, 160 °C, the amount of but-1-ene formed increases, and the stereoselectivity is reversed *i.e.* **1a** mainly gives (*Z*)-but-2-ene whereas the major product obtained from **2a** is (*E*)-but-2-ene. The reaction is now proceeding *via* a *syn* elimination (Scheme 1, Table 1).

To our knowledge, that is the first reported example where an inversion of the stereoselectivity in a thermally induced decomposition of an alcohol is observed. This intriguing result led us to investigate this thermal effect in greater detail. Bis(tributyltin)oxide formed during the elimination (intermolecular dehydration of tributyltin hydroxide) was suspected to act as a base and to give tributyltin alkoxides **1b** or **2b** by



Scheme 1

<sup>†</sup> Typical procedure: 0.720 g of **1a** (2 mmol) under nitrogen in a Schlenk tube connected to a gas burette was heated at 100 °C for 6 h. A quantitative amount of butenes was produced, which was analysed by vapour phase chromatography by comparison with authentic samples. In the experiments conducted under vacuum, the Schlenk tube was connected to another Schlenk tube maintained at -196 °C.

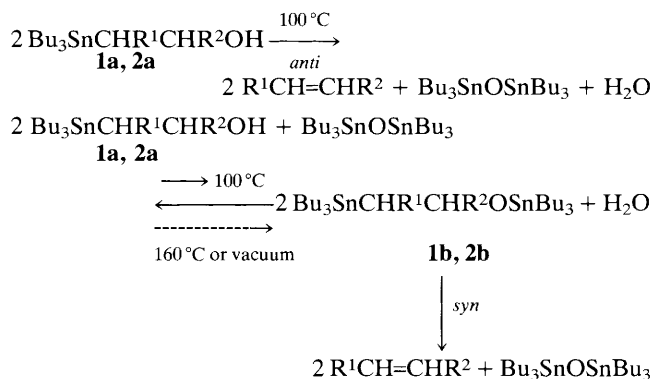
Table 1

Compound	Reaction conditions	But-1-ene (%)	(E)-But-2-ene (%)	(Z)-But-2-ene (%)
<b>1a</b>	100 °C, 6 h	2	89	9
<b>1a</b>	160 °C, 20 min	8	31	61
<b>1b</b>	100 °C, 3 h	2	8	90
<b>1b</b>	200 °C, 10 min	6	5	89
<b>1a</b>	100 °C, 6 h, 1 Torr	1	37	62
<b>2a</b>	100 °C, 6 h	—	10	90
<b>2a</b>	160 °C, 20 min	2	78	20
<b>2b</b>	100 °C, 3 h	3	93	4
<b>2b</b>	200 °C, 10 min	5	94	1
<b>2a</b>	100 °C, 3 h, 1 Torr	2	66	32

reaction with the alcohols **1a** or **2a** during the high temperature elimination (Scheme 2). Samples of **1b** and **2b** have been prepared by the reaction of **1a** or **2a** with stoichiometric amounts of dimethylaminotributylstannane, and subjected to thermolysis. At 100 °C, the process is more rapid than the decomposition of the corresponding alcohol and furnishes the *syn* elimination products (*Z*)-but-2-ene from **1b** or (*E*)-but-2-ene from **2b**. The same selectivity is observed at 200 °C. When the reaction is conducted under vacuum (1 Torr = 133.322 Pa) in order to eliminate the produced water and to promote the formation of the alkoxides, **1a** gives (*Z*)-but-2-ene and **2a** leads to (*E*)-but-2-ene. By thus simply running the thermolysis at atmospheric pressure or below, it is possible to drive the thermal decomposition of one 2-trialkylstannyl alcohol either to an alkene or its isomer.

To account for the reversal of selectivity observed in the thermolysis of the 2-trialkylstannyl alcohols between 100 and 160 °C, we suggest an explanation based on the formation of a tin alkoxide intermediate. At 100 °C, an *anti* elimination of 2-trialkylstannyl alcohols **1a** or **2a** occurs, with formation of bis(tributyltin)oxide and water which prevents the formation of tin alkoxides. At higher temperatures, water is eliminated from the reaction mixture allowing the formation of tributyltin alkoxides which then undergo a *syn* elimination.

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Scheme 2

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