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Preliminary communication

A NEW ROUTE TO VINYLTRIBUTYLTIN COMPOUNDS BY FLASH PYROLYSIS OF ALKYLTRIBUTYLTIN ACETATES

J. GEORGES DUBOUDIN,

Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux,
351, cours de la Libération, 33405 Talence (France)

MICHEL PETRAUD,

Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO),
Université de Bordeaux I, cours de la Libération, 33405 Talence (France)

MAX RATIER and BRUNO TROUVE

Laboratoire de Chimie Organique du Silicium et de l'Etain, associé au CNRS (UA 35),
cours de la Libération, 33405 Talence (France)

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Summary

Flash pyrolysis of alkyltributyltin acetates, at high temperatures (600—850°C) under a moderate vacuum provides a convenient route to vinyltin derivatives.

Vinylstannanes are useful and versatile synthetic intermediates, which can be converted with retention of configuration into vinyllithium derivatives by transmetalation with organolithium compounds [1]. However, only a limited number of preparation routes to vinylstannanes are available. Early reports mention the use of exchange reactions with Grignard [2,3] and organolithium [4—6] reagents. Another method involves hydrostannation of alkynes [7—9]. A more recent approach involves metalation of vinylic halides by triorganostannyl anions [10—13]. Recent communications [14,15] on pyrolytic generation of stannylated vinyl compounds prompt us to report our preliminary experiments in this field.

Pyrolysis of α-tributyltin acetates (derived from simple aromatic or aliphatic ketones), at 600 to 850°C and under reduced pressure (10^{-2} mmHg) gave vinylstannyl compounds, despite the weak bond dissociation energy values of the tin—carbon bond [16,17].

The synthetic sequence is shown in the following scheme:

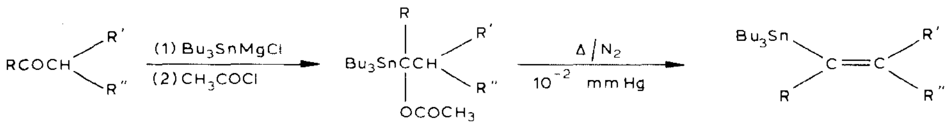

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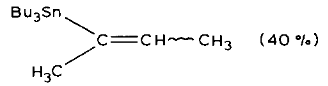
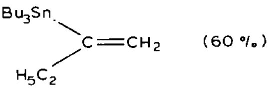
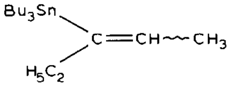
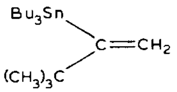
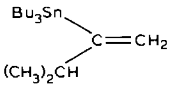
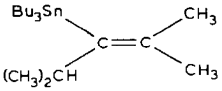
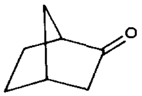
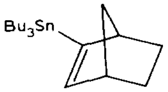
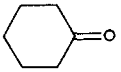
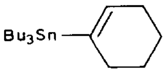
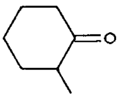
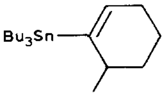
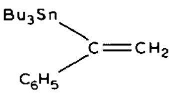
TABLE 1

PYROLYSIS OF α-TRIBUTYLTIN ACETATES [a]

Entry	Carbonyl compounds	T (° C)	Vinylstannanes	Yields [b]
1	$CH_3COC_2H_5$	650	 Z/E = 54/46 [c] 	76
2	$C_2H_5COC_2H_5$	750	 Z/E = 55/45 [c]	42
3	$(CH_3)_3CCOCH_3$	700		65
4	$(CH_3)_2CHCOCH_3$	700		49
5	$(CH_3)_2CHCOCH(CH_3)_2$	850		23
6		820		29
7		800		48
8		850		40
9	$C_6H_5COCH_3$	600		25

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[a] The pyrolysis tube was packed with broken silica. The sample was placed in a porcelain cup in the sublimation chamber at 250° C. [b] Isolated yields based on the amount of acetate used in the pyrolysis. [c] Determined by ^{13}C NMR analysis.

The reactions were carried out in a flash vacuum apparatus [18], with nitrogen as carrier gas, the emergent vapors being quenched on a Dewar cold finger. The results are shown in Table 1.

Our procedure offers two major advantages. First it allows a new access to substrates bearing the tin atom on the more substituted carbon (hydrostannation of alkynes leads mainly to the other regioisomer). Secondly, as shown by experiments 4 and 8 (see Table 1), the reaction can be regioselective (with exclusive production of the less substituted olefin).

Additional studies now in progress are aimed at use of this technique in the synthesis of functional compounds.

All compounds were characterized by ^{13}C and ^{1}H NMR spectroscopy. Proton magnetic resonance spectra were recorded on a Perkin—Elmer 60 MHz spectrometer and the ratio of *Z/E* regioisomers determined on a Bruker WH 90 operating at 22.63 MHz with $CDCl_3$ as solvent. HPLC analyses were performed with a Varian 5000 system (UV absorbance detector working at 220 nm; column C_{18} Varian Micropack MCH-10 (300 × 4 mm)). Tributylstannylmagnesium chloride was prepared by a standard procedure [19] from 0.11 mol of tributyltin hydride [20] and 56 ml of i-PrMgCl (1.26 *N*). The tributylstannyl acetates were obtained by in situ acetylation of tributylstannyl alcoholates [21]. Distillation under high vacuum (10^{-2} mmHg) followed by purification through a small column of Florisil gave the acetates in ca. 60% yield.

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