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Preliminary communication

Carbonyl olefination with α-stannyl ester enolates: a new synthesis of α,β-unsaturated esters

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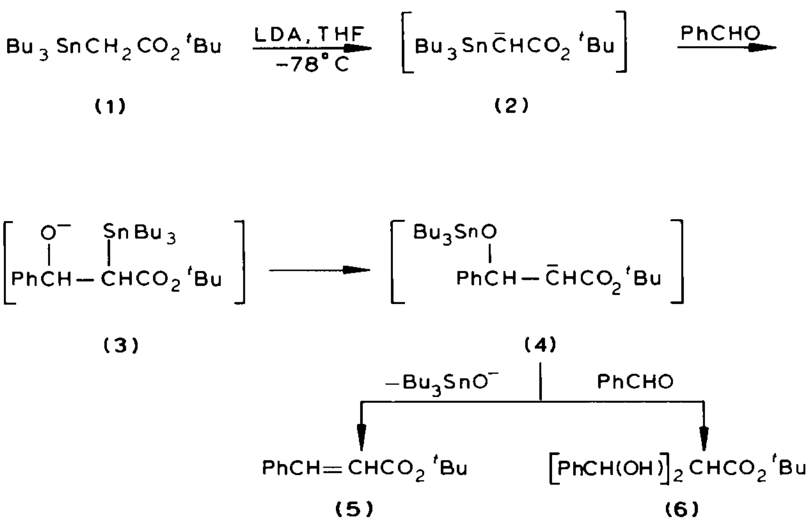
Abstract

The reaction of α-stannyl ester enolates with carbonyl compounds is described. α,β-Unsaturated esters are obtained in good yields. A reaction mechanism is proposed.

α-Silyl ester enolates react with aldehydes and ketones to give α,β-unsaturated esters [1]. This reaction has become an important method for the synthesis of this type of organic compounds [2]. In this communication we report that analogous carbonyl olefination are possible with α-stannyl esters [3], providing a new application of these organotin compounds in synthetic organic chemistry.

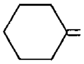
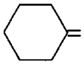
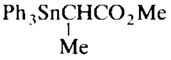
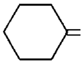
Addition of tert-butyl (tributylstannyl)acetate, **1** [3], to tetrahydrofuran (THF) solutions of lithium diisopropylamide (LDA) at −78 °C produces the lithium ester



Scheme 1.

Table 1

Reaction of α-stannyl esters with carbonyl compounds

Ester [a]	Carbonyl compound	Product [a]	% Yield [b]($E:Z$ ratio) [c]
$Ph_3SnCH_2CO_2{}^tBu$	benzaldehyde	$PhCH{=}CHCO_2{}^tBu$	82(>95:<5)
	cyclohexanone	 $=CHCO_2{}^tBu$	73
	2-phenlypropanal	$Ph(Me)CH-CH{=}CHCO_2{}^tBu$	86(>95:<5)
$Ph_3SnCH_2CO_2Me$	benzaldehyde	$PhCH{=}CHCO_2Me$	68(>95:<5)
	cyclohexanone	 $=CHCO_2Me$	78
	2-phenylpropanal	$Ph(Me)CH-CH{=}CHCO_2Me$	69(>95:<5)
 $Ph_3Sn\underset{\textstyle Me}{\underset{\mid}{C}}HCO_2Me$	benzaldehyde	$PhCH{=}C(Me)CO_2Me$	78(90:10)
	cyclohexanone	 $=C(Me)CO_2Me$	79
	2-phenylpropanal	$Ph(Me)CH-CH{=}C(Me)CO_2Me$	68(2:8)
$Bu_3SnCH_2CO_2{}^tBu$	benzaldehyde	$PhCH{=}CHCO^tBu$	60(>95:<5)

[a] All new compounds have spectral and analytical data in agreement with the proposed structure. [b] Isolated yield after purification by flash chromatography on silica gel. [c] Ratio of Isomers estimated by HPLC

enolate **2** (Scheme 1). Subsequent treatment with one equivalent of benzaldehyde gave a mixture of two major products: the expected product tert-butyl cinnamate, **5**, in 60% yield, and tert-butyl bis(α-hydroxybenzyl)acetate, **6**, in 12% yield [4*]. By inverse addition to five equivalents of benzaldehyde, the yield of **6** was increased to 22%.

Conceivably, compound **6** could be formed by reaction of benzaldehyde with β-stannyloxy enolate, **4**, which in turn was formed from β-oxido stannane, **3**, by 1,3-migration of tin from carbon to oxygen [5*]. The isolation of **6** constitutes strong evidence in favor of **4** as a key intermediate in these reactions [6*].

We also examined this reaction with α-triphenylstannyl ester enolates. The starting esters were conveniently prepared by a modification of our published procedure [3]. Thus, triphenylstannylation of carboxylic esters with the aid of LDA afforded the corresponding C-stannylated products in high yields.

Reaction of α-triphenylstannyl ester enolates with carbonyl compounds gave the desired α,β-unsaturated esters. The results are shown in Table 1. As can be noted, the yields are good and the reaction proceeds with both aldehydes and ketones. High *E* selectivity is observed which is consistent with the proposed mechanism (see Scheme 1). Elimination of the β-stannyloxy group in intermediate **4** should occur from the conformation having less steric interactions.

α-Silyl esters have been used for the synthesis of α,β-unsaturated esters for many years [1,2]. However, access to α-silyl esters by direct C-silylation of ester enolates is possible only with tert-butyl acetates [7] or by the use of the rather expensive reagent diphenylmethylchlorosilane [8]. In contrast, a wide variety of

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

α-stannyl esters are readily available in high yields by C-stannylation of lithium ester enolates with either tributyl- or triphenyltin chloride [3]. Therefore, this new synthesis of α,β-unsaturated esters, from carbonyl compounds and α-stannyl esters, has distinct advantages. The results described here offer both a convenient synthetic alternative and an incentive to explore new uses of α-stannyl esters in organometallic chemistry.

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References

1 K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto and H. Nozaki, J. Am. Chem. Soc., 96 (1974) 1620; S.L. Hartzell, D.F. Sullivan and M.W. Rathke, Tetrahedron Lett., (1974) 1403; G.L. Larson, C. Fernández de Kaifer, R. Seda, L.E. Torres and J.R. Ramírez, J. Org. Chem, 49 (1984) 3385 and references therein.
2 For applications to the synthesis of α-heterosubstituted α,β-unsaturated esters see: A. Zapata, C.R. Fortoul and C.A. Acuña, Synth. Commun., 15 (1985) 179; A. Zapata and F.G. Ferrer, Synth. Commun., 16 (1986) 1611; T.H. Chan and M. Moreland, Tetrahedron Lett., (1978) 515; S.L. Hartzell and M.W. Rathke, Tetrahedron Lett., (1976) 2737; S. Inoue, Y. Sato and T. Suzuki, Organometallics, 7 (1988) 739.
3 A. Zapata and C.A. Acuña, Synth. Commun., 14 (1984) 27 and references therein.
4 Besides having spectral and analytical data in accord with the proposed structure, the identity of compound **6** was confirmed by mixed melting point determination with an independently synthesized sample.
5 Metallotropic rearrangements of α-stannyl carboxylic esters to the corresponding triorganotin enolates are known: A.N. Kashin, M.L. Tulchinsky and I.P. Beletskaya, J. Organomet. Chem., 292 (1985) 205 and references therein.
6 Similar intermediates have been isolated from analogous reactions with silicon compounds: S. Inoue and Y. Sato, Organometallics, 5 (1986) 1197 and references therein.
7 M.W. Rathke and D.F. Sullivan, Synth. Commun., 3 (1973) 67.
8 G.L. Larson and L.M. Fuentes, J. Am. Chem. Soc., 103 (1981) 2418.