

Preliminary communication

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

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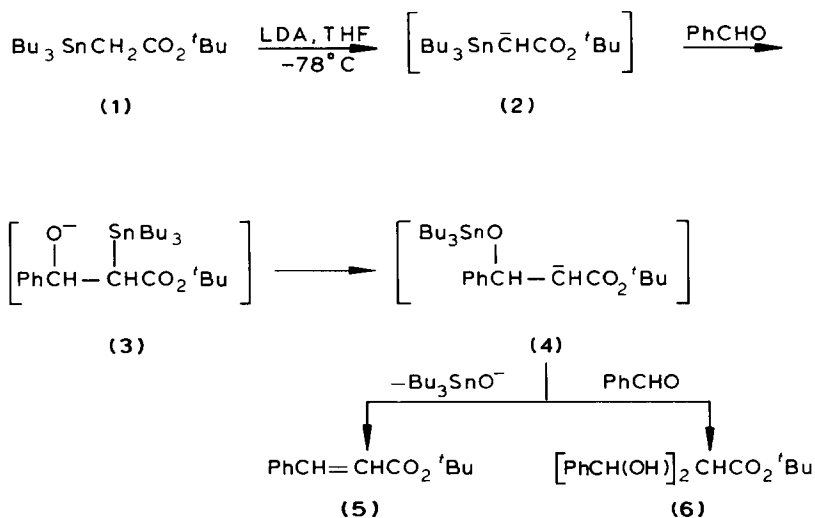
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Abstract

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 (<i>E</i> : <i>Z</i> ratio) ^c
Ph ₃ SnCH ₂ CO ₂ ^t Bu	benzaldehyde	PhCH=CHCO ₂ ^t Bu	82(> 95:< 5)
	cyclohexanone	 =CHCO ₂ ^t Bu	73
Ph ₃ SnCH ₂ CO ₂ Me	2-phenylpropanal	Ph(Me)CH-CH=CHCO ₂ ^t Bu	86(> 95:< 5)
	benzaldehyde	PhCH=CHCO ₂ Me	68(> 95:< 5)
	cyclohexanone	 =CHCO ₂ Me	78
Ph ₃ SnCHCO ₂ Me Me	2-phenylpropanal	Ph(Me)CH-CH=CHCO ₂ Me	69(> 95:< 5)
	benzaldehyde	PhCH=C(Me)CO ₂ Me	78(90:10)
	cyclohexanone	 =C(Me)CO ₂ Me	79
Bu ₃ SnCH ₂ CO ₂ ^t Bu	2-phenylpropanal	Ph(Me)CH-CH=C(Me)CO ₂ Me	68(2:8)
	benzaldehyde	PhCH=CHCO ^t Bu	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 -stannoxy 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 -stannoxy 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

* 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

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- 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.
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