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Reactivity of α-Metal(group 4) Esters. Lewis Acid Mediated Reactions of α-Triphenyltin Esters with Aldehydes and Acetals

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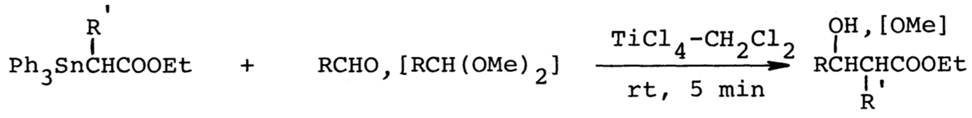
Ethyl triphenylstannylacetate and ethyl α-triphenylstannylpropionate reacted with aldehydes and acetals to give β-hydroxy and β-alkoxy esters at room temperature in the presence of $TiCl_4$ in moderate yields. Under these conditions ethyl triphenylgermylacetate and ethyl trimethylsilylacetate did not work.

The improvement of versatile reactions for carbon-carbon bond formation is an important framework of synthetic organic chemistry. The Reformatsky reaction1) is widely recognized as an effective synthetic tool and its improvements are being continued up to date.2) Reformatsky-type reactions using other α-metallic esters3) are not so much, compared with similar reactions using α-metallic ketones.4) The study of relative reactivity of α-metal(group 4) esters toward carbonyl compounds is of interest to find out more facile preparations of β-hydroxy esters, but its systematic comparisons have not been done yet.

The addition reaction at room temperature of ethyl α-triethylstannylacetate was limited to the compounds having carbonyl group polarized by strong electron withdrawing group (e.g. CCl_3CHO, C_6F_5CHO).3a) In this communication, we report that Reformatsky-type reactions using α-triphenyltin esters5) with aldehydes and acetals are smoothly promoted by Lewis acid, especially titanium tetrachloride, at room temperature.



$$\mathrm{Ph_3Sn\overset{R'}{C}HCOOEt} \quad + \quad \mathrm{RCHO,[RCH(OMe)_2]} \xrightarrow[\text{rt, 5 min}]{\mathrm{TiCl_4-CH_2Cl_2}} \mathrm{R\overset{OH,[OMe]}{C}H\underset{R'}{C}HCOOEt}$$

In a typical experiment; to a solution of titanium tetrachloride (1.5 mmol) in dichloromethane was added dropwise a mixture of ethyl triphenylstannylacetate (1.5 mmol) and benzaldehyde (1.5 mmol) in dichloromethane at room temperature. After stirring for 5 min, the reaction mixture was quenched with water. (The reaction with acetal was first quenched with methanol.) After usual work-up, purification by flash column chromatography gave the desired β-hydroxy(or methoxy) ester; 72%. Further the triphenyltin moiety was economically recovered as triphenyltin chloride in all runs; which is presumably produced by interaction with $TiCl_4$ in the reaction.

The products were obtained in moderate yields and these reactions showed

Table 1. Titanium tetrachloride mediated reactions of Ph_3SnCH_2COOEt 1 and $Ph_3Sn(CH_3)CHCOOEt$ 2 with aldehydes and acetals[a)]

Run	α-Tin ester	Aldehyde, Acetal	Isolated yield/%	Selectivity
1	1	i-PrCHO	76	
2	1	PhCHO	72	
3	1	$i\text{-}PrCH(OMe)_2$	55	
4	1	$PhCH(OMe)_2$	64	
5	2	i-PrCHO	63	2 : 1[b)]
6	2	PhCHO	74	1.6 : 1[b)]
7	2	$PhCH(OMe)_2$	65	3.2 : 1[b)]
8	1	PhMeCHCHO	69	1.6 : 1[c)]
9	1	$PhMeCHCH(OMe)_2$	64	3.1 : 1[c)]

a) Reaction conditions (see text); rt, 5-10 min. b) Erythro/threo ratios determined from their ^1H-NMR spectra, according to Ref. 6. c) Cram/anti-Cram ratios determined from their ^1H-NMR spectra, according to Ref. 7.

erythro- and Cram-selectivities, as summarized in Table 1. Other Lewis acids (e.g. $BF_3{\cdot}OEt_2$, $SnCl_4$) did not effectively accelerate these reactions. A long-time reaction gave complex products. In addition, Me_3SiCH_2COOEt and Ph_3CH_2COOEt were unexpectedly inert toward Lewis acid conditions described in this text in contrast with α-silyl and α-germyl ketones.[4b,c)]

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