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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 reaction[1] 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 esters[3] 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 esters[5] with aldehydes and acetals are smoothly promoted by Lewis acid, especially titanium tetrachloride, at room temperature.

$$Ph_3SnCH(R')COOEt + RCHO, [RCH(OMe)_2] \xrightarrow[rt,\ 5\ min]{TiCl_4\text{-}CH_2Cl_2} RCH(OH, [OMe])CH(R')COOEt$$

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 ^{1}H-NMR spectra, according to Ref. 6. c) Cram/anti-Cram ratios determined from their ^{1}H-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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