

Reactivity of β -Stannylketones. Elimination vs. Substitution

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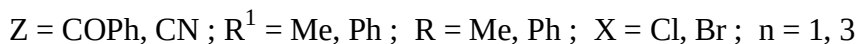
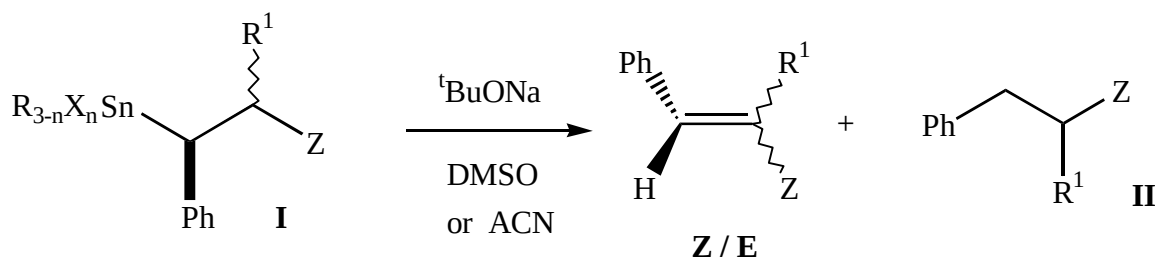
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Abstract: In the present work we report the results obtained in the reaction of β -stannylketones (**I**) with *t*-BuONa in dimethylsulfoxide (DMSO) and acetonitrile (ACN) as solvents. The reaction mechanisms probably involved are proposed.

Introduction

In the reaction of β -functionalized organotin compounds (**I**) with *t*-BuONa in *t*-BuOH there is a competition between an elimination reaction [(E1cB)_R], leading to olefins with high diastereoselectivity, and a nucleophilic substitution reaction yielding the reduction product (**II**) [1]. Now we report on the reactions of β -stannylketones (**I**) with *t*-BuONa in DMSO and ACN in order to compare the reactivity in these solvents.



Experimental

Anhydrous solvents and sublimated *t*-BuONa were used. The β -stannylketones were synthesized in our laboratory [2-3]. The reaction mixtures were analysed by CGL. The reaction conditions are detailed in the Table.

Results and Discussion

The results summarised in the Table show that these reactions lead to higher yields in shorter reaction times, depending on the substrates. Thus, while β -stannylketones carrying electron-withdrawing groups attached to tin lead to the elimination product in high yield, β -trialkylstannylketones give mainly the reduction product.

Table. Reactions of $R_{3-n}X_nSn-CH(Ph)-CH(R^1)-COPh$ with $tBuONa^a$.

N°	R^1	$R_{3-n}X_nSn$	DMSO	ACN
			% Elim (Z/E)	% Elim (Z/E)
1	Me	Ph_3Sn	58 (10/90) ^b	39 (1/99) ^c
2	Me	Ph_3Sn	86 (19/81) ^b	85 (0/100) ^c
3	Me	Ph_2BrSn	84 (10/90)	83 (0/100)
4	Me	Me_3Sn	- ^d	37 (30/70) ^d
5	Me	Cl_3Sn^e	92 (0/100)	85 (0/100)
6	Me	Cl_3Sn^f	81 (100/0)	80 (100/0)
7	Ph	Me_3Sn^e	- ^d	76 (16/84) ^c
8	Ph	Me_3Sn^f	- ^d	58 (17/83) ^c
9	Ph	Cl_3Sn^g	98 (89/11)	69 (90/10)

^aSubstrate/base ratio 1/1.1 Similar results are obtained from both *erythro* and *threo* isomers; ^bStarting substrate is recovered like a diastereoisomeric mixture; ^cNo isomerization of the starting substrate was observed; ^dHigh yield of the reduction product; ^e*Erythro* isomer; ^f*Threo* isomer; ^g*Erythro/threo* 13/87.

The stereochemical results show that, in most cases, these reactions are stereoconvergent. The same ratio Z/E is obtained independently of the configuration of the starting substrate. (Table, entries 1-4, 7 and 8). Taking into account the stereochemistry observed we are able to say that, probably, the elimination reaction goes through an $(E1cB)_R$ mechanism in DMSO and through an $(E1cB)_I$ in ACN.

On the other hand, β -trichlorostannylketones (Table, entries 5, 6 and 9) give high yields of olefins through a stereospecific elimination reaction. Two possible mechanisms could be proposed to explain these results: a concerted E2, or an $(E1cB)_I$ in which, because of electronic interactions between the trichlorostannyl group and the oxygen atom, the intermediate carbanions are not interconvertibles.

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References and Notes

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