

Addition of Organotin Anions to α,β -Unsaturated Nitriles

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Abstract: The addition reaction of triorganotin anions to α,β -unsaturated nitriles leads to α -alkyl- β -stannylnitriles with high diastereoselectivity.

Introduction

The reaction of triphenyl- and trimethyltin anions with α,β -unsaturated ketones in acetonitrile as solvent is rather instantaneous and leads with high diastereoselectivity and in nearly quantitative yields, to β -stannylketones [1]. On the other hand, there are few reports in the literature concerned with the reaction of triorganostannyl anions with α,β -unsaturated nitriles which would lead to β -stannylnitriles through an 1,4-addition. Taking into account the application of these adducts as intermediates in organic synthesis [2,3] we started some studies on the reaction of triphenyl- and trimethyltinpotassium with compounds **I**, **II** and **III**, in acetonitrile (ACN) as solvent.

Experimental

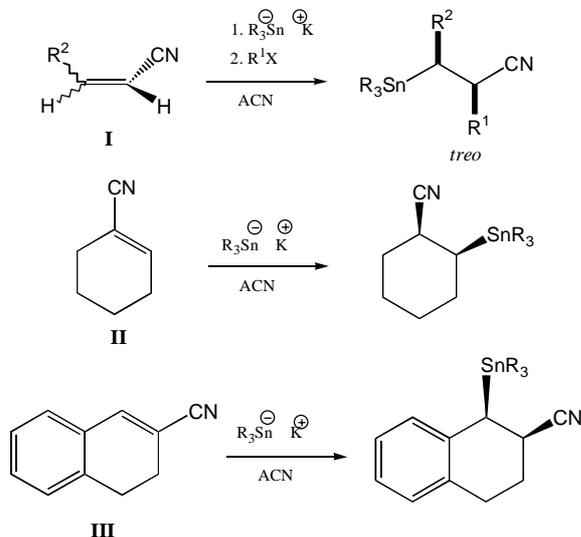
To a solution of the stannyl anion (from the reaction between an organotin hydride and potassium *tert*-butoxide [1]) was added a solution of the nitrile in ACN. The reaction was quenched by the addition of water or an alkyl halide and then worked as usual. The adducts were purified by column chromatography, distillation or recrystallization and characterized by ^1H and ^{13}C NMR.

Results and Discussion

The experimental results indicate that the addition reaction to α,β -unsaturated nitriles is partially inhibited by the presence of one substituent in the α - or β - positions. Thus, while acrylonitrile lead to the adduct in an 85% yield, metacrylonitrile and 2-butenonitrile gave lower yields (62% and 43% respectively). On the other hand, the addition is highly inhibited by the presence of α - and β -substituents in open chain olefinic systems (2,3-diphenylpropenenitrile gave a null reaction) but not in cyclic ones (1-cyanocyclohexene and 2-cyano-3,4-dihydronaphthalene gave 63% and 67% yield, respectively).

The stereochemical results show that these reactions are highly diastereoselective. Thus, we only

obtained pure *threo* isomers from open chain nitriles and *cis* adducts from the cyclic ones. Trapping the intermediate carbanions with different alkyl halides would allow the diastereoselective synthesis of a large number of α -alkyl- β -stannyl nitriles.



The diastereocontrol observed in the addition of stannyl anions to activated nitriles arises from stereoelectronic and steric effects.

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References and Notes

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3. Murray, A.P. Thesis, 1999.