

γ -Tributylstannyl- β -Metallated Acrolein : a versatile synthon[#]

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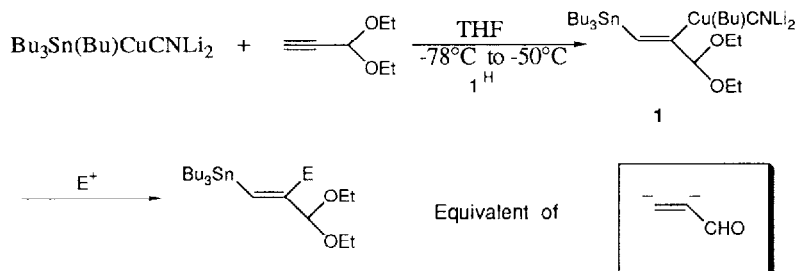
Key words : stannocupration, d^2 , d^3 acrolein equivalent, diethoxypropyne, vinyl tin.

Abstract : The stannocupration of the diethoxypropyne affords very selectively the title compound which can be alkylated with various electrophiles.

During these recent years, organic reagents that possess two nucleophilic centers¹, two electrophilic centers², or one nucleophilic and one electrophilic sites³, have become increasingly important in organic synthesis. Incorporation of these species into substrate molecules by simultaneous or sequential deployment of the two reactive sites often results in short, efficient conversions of structurally rather simple starting materials into significantly more complex, usefully functionalized products. These "bifunctional conjunctive reagents"⁴ or "multiple coupling reagents"⁵ have been prepared and used effectively in organic synthesis. In parallel to the carbocupration reaction⁶, cuprate reagents derived from silyl⁷ and stannyl metals^{8,9} have been prepared and added to carbon-carbon triple bonds. Although the hydrostannation reaction of alkynes provides a simple route to alkenyl stannanes, it is generally not stereoselective¹⁰. The addition of trialkylstannylcopper and cuprate to 1-alkynes and to α,β -acetylenic esters and amides has been exploited largely in recent years¹¹. In spite of its synthetic utility, the mechanism of this reaction is still poorly understood. The most widely accepted hypothesis, advanced by Piers, suggests that this reaction proceeds via a reversible addition to yield equilibrium mixtures of alkyne and adduct^{8d}, which may be driven to product only by the presence of a protic solvent that hydrolyzes the presumptive vinylcopper intermediate but not the stannylcuprate⁸. In the case of propargylic ethers^{8b}, this reaction does not require the presence of a proton source but the regioselectivity of the addition is relatively poor.

Herein, we report a readily accessible functionalized organotin reagent prepared by stannocupration of the available 3,3-diethoxypropyne¹², to afford a vinylic cuprate which can be alkylated with various electrophiles (scheme 1) and behaves as a 3-stannyl d^2 acrolein, or as a d^2 , d^3 acrolein synthon¹³.

[#] These results must be compared with those obtained independently by I. Beaudet, J.-L. Parrain, J.-P. Quintard (accompanying paper)



Scheme 1

Table 1 illustrates the diversity of electrophiles which, upon exposure to the presumed mixed reagent **1**, afford good isolated yields of 3-tributylstannyl-2 substituted-1,1-diethoxypropenes

Table 1 : Reaction of stannyl vinyl copper **1** with electrophile

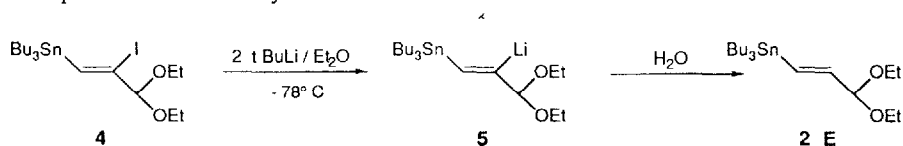
Entry	Electrophile	Products(a)	Yields(b) %
1	MeOH		95
2	MeOD		93
3	I ₂		72
4	$\text{C}\equiv\text{C}-\text{COOMe}$	 E / Z = 87% / 13%	70
5			78

(a) Isolated pure products gave satisfactory IR, ¹H, ¹³C and ¹¹⁹Sn NMR data.

(b) Yield of products isolated by chromatography on silica gel.

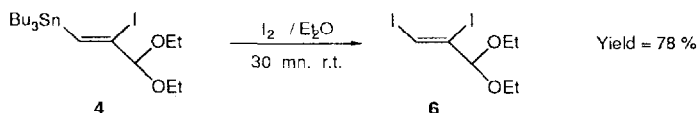
As shown in the Table 1, the Bu₃Sn ligand is transferred exclusively to diethoxyacetyne. Moreover, the stannocupration reaction leads to only one isomer (entry 1). This regioisomer may arise from the complexation of the copper atom (or its associated salts) with the oxygens of the acetal¹⁴. Addition of an equimolar amount of solid iodine to the solution of the alkenyl cuprate affords the corresponding alkenyl iodide **4** in high yield (entry

3). By halogen-metal exchange¹⁵, at low temperature in Et₂O, **4** is converted to the β-stannyllithium derivative **5**, without participation of the tin carbon bond. The latter affords, after hydrolysis, the vinyl tin compound with pure E stereochemistry :



Scheme 2

The alkenyl cuprate derivative can also react in 1-4 fashion with methyl propiolate to give the 1-3 diene with a good yield (entry 4). In a similar way, reagent **1**, can be allylated by allyl bromide to give the 1-4 diene (entry 5). On the other hand, alkenyl stannanes have been utilized for a variety of synthetic applications¹⁶. The palladium catalyzed coupling reactions of vinyl halides with alkenyl stannanes¹⁷, the facile transmetalation reaction with alkyl lithiums or dialkylcuprates have been nicely exploited by Quintard *et al*¹⁸, in the study of d³ acrolein equivalents. Along these lines, the treatment of compound **4** with iodine affords the corresponding 2,3-diiodo 1,1-diethoxypropene **6**, with retention of configuration of the vinyl group¹⁹.



Scheme 3

The possibility of independently applying a variety of reactions of alkenylcuprates and alkenylstannanes to this bifunctional adduct **1** provides many opportunities for subsequent synthetic elaborations.

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