

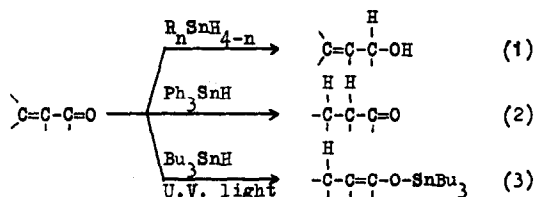
REACTION OF ORGANOTIN HYDRIDES WITH α,β -UNSATURATED KETONES

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The reaction of α,β -unsaturated aldehydes and ketones with organotin hydrides have been studied intensively by Kuivila and Beumel^{1,2} and by Valade and Pereyre^{3,4}. Whereas in the first reports on this subject^{1,2,5} selective reduction of the carbonyl function (1) was the only reaction observed, it has been shown more recently³ that the reaction of organotin monohydrides with mesityl oxide takes a different course. Triphenyltin hydride was found to reduce the carbon-carbon double bond (2), whereas tributyltin hydride, under the influence of U.V.-irradiation, yielded mainly the 1,4-adduct (3).



While our investigations of the reaction of organotin hydrides with carbonyl derivatives were in progress, it was reported in a recent study⁴ that reactions of triphenyl- and tributyl-tin hydride with a series of α,β -unsaturated aldehydes and ketones followed exclusively pathways (2) and (3), respectively. Some of our independent observations in this area are reported in the present communication.

TABLE I

Reaction of Organotin Hydrides with Some α,β -Unsaturated Ketones
$$R_3SnH + C=C-C=O \longrightarrow \begin{array}{c} H \\ | \\ -C-C-C-O-SnR_3 \\ I \end{array} + \begin{array}{c} H \quad H \\ | \quad | \\ -C-C-C=O \\ II \end{array} + R_3Sn-C \begin{array}{c} H \\ | \\ -C-C=O \\ III \end{array}$$

Ketone	Tin Hydride	Molar Ratio Ketone:Hydride	Reaction conditions	Yield %	Molar Ratio I : II : III
Chalcone ^c	Bu ₃ SnH	1:1	5 hrs., 70°	90	90: 10 ^a : -
"	"	1:1	6 hrs., 70°	80	100: 0: -
"	Ph ₃ SnH	3:1	3 hrs., 55°	70	40: 60: -
"	"	1:2	3 hrs., 55°	90	40: 60: -
"	"	1:3	{ 3 hrs., 55° 5 hrs., 55° ^b	{ 75 80	{ 50: 50: - 0:100 ^b : -
"	Ph ₂ SnH ₂	1:1	3 hrs., 55°	55	0:100: -
"	"	1:2	3 hrs., 55°	45	0:100: -
PhVi Ketone ^d	Bu ₃ SnH	1:1	6 hrs., 55°	60	95: 5 ^a : -
"	"	3:4	20 hrs., 55°	45	85: 15 ^a : -
"	Ph ₃ SnH	3:4	3 hrs., 55°	60	70: 30: -
"	"	1:2	4 hrs., 55°	85	0:100: -
"	Ph ₂ SnH ₂	3:4	2 hrs., 55°	25	0:100: -
MeVi Ketone ^e	Bu ₃ SnH	1:1	12 hrs., 55°	0	-
"	Ph ₃ SnH	2:1	3 hrs., 55°	80	- : 45 :55
"	"	1:1	4 hrs., 55°	60	- : 35 :65
"	"	1:2	3 hrs., 55°	80	- : 35 :65
"	"	1:2	2 hrs., 55°	65	- : 30 :70
"	Ph ₂ SnH ₂	1:1	1 hr., 55°	40	- :100 : 0
"	"	1:1	3 hrs., 55°	35	- :100 : 0

^a The presence of compound II in these reaction mixtures most probably is the result of hydrolysis of compound I.

^b NMR spectrum run after standing overnight.

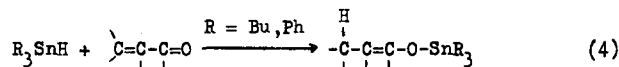
^c 1,3-Diphenylpropenone.

^d Phenyl vinyl ketone.

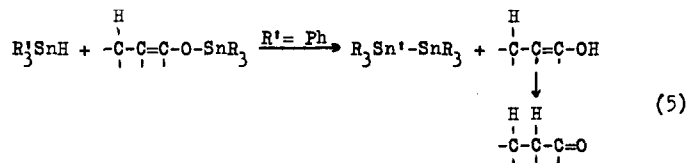
^e Methyl vinyl ketone.

The results of our investigation of the reaction of tributyl- and triphenyl-tin hydride and of diphenyltin dihydride with chalcone (1,3-diphenylpropenone), phenyl vinyl ketone and methyl vinyl ketone in the absence of solvents and catalysts are presented in Table I. In these experiments the structures and yields of the several products were derived from NMR spectra of the reaction mixtures, run after completion of the reactions. As appeared from these spectra the expected α,β -unsaturated alcohols, if present at all, were formed in negligible amounts. Similar results were obtained upon reacting diphenyltin dihydride in wet ether with these ketones, following the procedure described by Kuivila and Beumel. For example, the NMR spectrum of the reaction product from diphenyltin dihydride and chalcone showed intensive signals due to hydrochalcone (reduction of C=C, yield ~ 40%), whereas only weak signals arising from chalcol (reduction C=O, yield < 10%) were observed.

As appears from Table I the primary step in the reaction of both tributyltin hydride and triphenyltin hydride with chalcone and phenyl vinyl ketone is 1,4-addition across the unsaturated system:



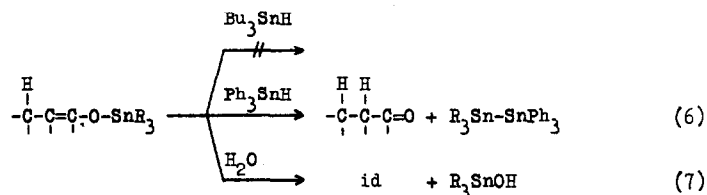
Depending on the nature of the organotin hydride employed, a subsequent hydrogenolysis reaction may occur, followed by a rearrangement of the vinylalcohol formed:



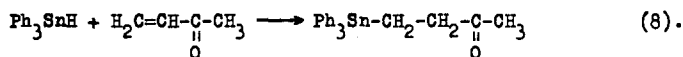
Thus, reduction of the carbon-carbon double bond is the overall result of a hydrostannation reaction (4) followed by a hydrogenolysis

reaction (5). The latter reaction has previously been shown⁶ to proceed by an electrophilic attack of the hydride hydrogen on oxygen. Since tributyltin hydride, in contrast to triphenyltin hydride, is a poor electrophile, reactions involving tributyltin hydride under our conditions stop at the 1,4 addition stage.

Further proof for this point of view was obtained from hydrogenolysis experiments. Upon heating the 1,4-adducts from triphenyltin- and tributyltin hydride with tributyltin hydride for several hours the saturated ketones were formed in very small amounts only. On the other hand, the adducts are cleaved easily by triphenyltin hydride (6) and by water (7). As a result of electronic and steric effects the hydrogenolysis of the 1,4-adducts from chalcone proceeds more slowly than that of the 1,4-adducts from phenyl vinyl ketone. Most probably the reduction products reported in experiments involving tributyltin hydride are the result of unintentional hydrolysis of the 1,4-adducts.



In the reaction of triphenyltin hydride with methyl vinyl ketone both reduction of and 1,2-addition (8) across the carbon-carbon double bond was observed. Obviously, the hydrogenolysis reaction (5) is much faster than the 1,4-addition reaction (4). Tributyltin hydride does not add under the conditions employed.



In conclusion, organotin monohydrides add mainly in 1,4-fashion to

the α,β -unsaturated ketones investigated. Whereas the reaction stops at this stage with tributyltin hydride and presumably with other trialkyltin hydrides as well, subsequent hydrogenolysis occurs in the case of triphenyltin hydride. It is reasonable to expect that the same holds true for other α,β -unsaturated ketones and for α,β -unsaturated aldehydes.

All attempts to reproduce earlier results ^{1,2,5}, i.e. exclusive reduction of the carbonyl group of α,β -unsaturated ketones by triphenyltin hydride and diphenyltin dihydride, have been unsuccessful. This does not exclude that under different conditions the α,β -unsaturated alcohols may be obtained. It should be noted that reduction of the carbonyl group followed by a rearrangement of the α,β -unsaturated alcohol ⁷ thus formed, will also yield the saturated ketone. Obviously such a mechanism does not occur in the case of triphenyltin hydride.

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