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The Ionic Reduction of Vinyl Stannanes

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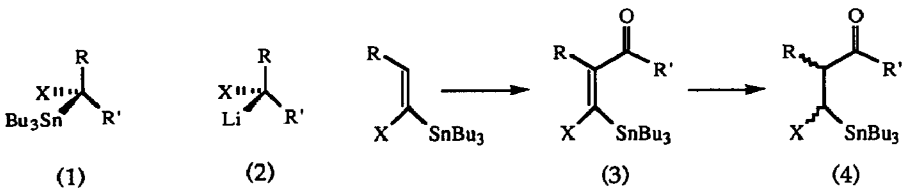
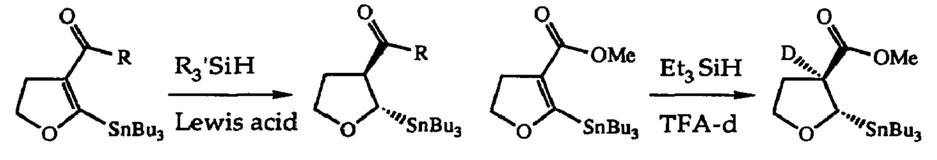
Abstract: *The ionic reduction of a variety of β-stannylacrylates is reported.*

The use of α-heterofunctionalised organostannanes (1) as masked forms of α-heterofunctionalised carbanions (2) continues to attract much attention[1]. A variety of methods are now available for the synthesis of unfunctionalised organostannanes bearing α-oxygen[2], -nitrogen[3], -sulphur[4], -selenium[5] or -silicon[6] substituents although *general* approaches for the preparation of functionally complex systems have yet to be developed. We recently[7] described a general method for the preparation of β-trialkylstannylacrylates (3) **Scheme**, which we considered could serve as precursors to a variety of functionalised organostannanes (4). The development of a simple regime for the reduction of the acrylates (3) is the subject of this *Letter*.



Scheme

The reduction of vinyl stannanes is generally fraught with difficulties which stem primarily from the innate reactivity of the vinyl C-Sn bond. As a consequence few general methods exist[8] for the execution of this seemingly simple sequence. Our initial investigations concentrated upon the reduction of the dihydrofuran derivative (5) as a test substrate, which unfortunately failed to undergo reaction with a variety of reducing agents known to effect conjugate reduction of α,β-unsaturated carbonyl compounds. It is well known[9] that "push-pull" olefins can be reduced using "ionic reducing" agents and we therefore attempted to reduce the acrylate (5) with triethylsilane in the presence of a suitable Lewis acid. To our delight, exposure of the acrylate (5) to triethylsilane (10 eq.) and boron trifluoride etherate[10] (2 eq.) in dichloromethane at -78°C and then allowing the reaction mixture to warm up to room temperature over a period of 4 hours resulted in the isolation of the diastereoisomerically pure *trans*-disubstituted tetrahydrofuran[11,12] (6) in good isolated yield (71%) In order to delineate the effect of Lewis acid upon the course of this reaction, the reduction sequence was repeated in the presence of TMS-triflate (2 eq.), trifluoroacetic acid, (TFA) (2 eq.) and acetic acid (2 eq.) using an excess of the silane (10 eq.); **Table** {entries 2 to 4). In the case of TFA and TMS-triflate reduction was complete in greatly reduced reaction times (30 minutes whilst warming up from -78°C to 0°C and 60 minutes at -78°C respectively) and afforded near quantitative yields (96-98%) of *isolated* product; reaction in the presence of acetic acid merely afforded starting material. Of note in all these reduction reactions was the isolation of little, if any, protodestannylated products. Reduction of the stannane (5) with triethylsilane (10 eq.) in the presence of deutereo-TFA (2 eq.) afforded the stannane (7) in excellent chemical yield (95%) with >90% incorporation at C3. Reduction of the vinyl stannane (5) with triphenylsilane[13] again proceeded smoothly although on this occasion higher yields were observed when the reduction sequence was conducted in the presence of TMS triflate (74%) rather than TFA (54%).



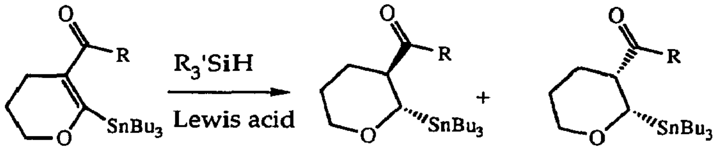
(5), R=OMe
(10), R=OBn
(14), R=NHTs

(+/-)
(6), R=OMe
(12), R=OBn
(15), R=NHTs

(5)

(+/-) (7)

In the case of the dihydropyran derivative (8), the nature of the Lewis acid additive had a profound effect upon the yield of the reduction sequence. Under optimised conditions reduction of the ester (8) with Et_3SiH-TMS triflate afforded the *trans*-product ((9); $J_{2,3}$ = 11 Hz) as a single diastereoisomer in excellent isolated yield (87%). Much reduced yields were observed when alternate Lewis acids e.g. $BF_3.OEt_2$ were employed. It is noteworthy that the benzyl esters (10) and (11) undergo clean reduction (to (12) and (13) respectively in 61% and 64% yield) without any sign of deprotection .



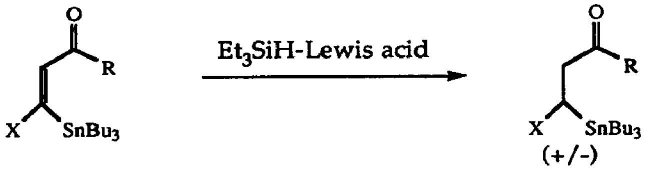
(8), R=OMe
(11), R=OBn
(16), R=NHTs

(+/-)
(9), R=OMe
(13), R=OBn
(17), R=NHTs

(+/-)
(18), R=NHTs

Curiously, whereas the tosamide (**14**) underwent very rapid reduction to the stannane (**15**) (Et_3SiH-TMS triflate or TFA; 80% and 83% yield respectively), the analogous dihydropyran derivative (**16**) underwent reduction to the tosamide (**17**) much more sluggishly and could not be coaxed to proceed to completion; after prolonged reaction times the *trans*-isomer ((**17**); $J_{2,3}$ = 7.2 Hz) was isolated in 41% yield together with a small amount (0.5%) of the *cis*-isomer ((**18**); $J_{2,3}$ = 2.2 Hz).

The reduction of acyclic systems such as (**19**) and (**20**)) was also briefly investigated. The exact choice of activating agent used in these reactions was again somewhat substrate dependent. Whereas the β-stannylacrylate (**19**) underwent rapid reduction (1 hr. at -78^{o}C) to the corresponding propionate (**21**) using TMSOTf-Et_3SiH, the thioenolether (**20**) underwent reduction to the propionate (**22**)[14] using $BF_3.OEt_2$ in conjunction with Et_3SiH albeit, over a much longer reaction time (4 days at room temp.) (**Table**, entries 16 to 19).



(19), X=R=OEt
(20), X=SPh; R=OMe

(21), X=R=OEt
(22), X=SPh; R=OMe

Entry	Vinyl stannane	Lewis or Protic acid	Reaction conditions	Product	Yield
1	(5)	$BF_3.OEt_2$	Et_3SiH; -78^{o}C 1hr; rt 3hrs.	(6)	71%
2	(5)	TFA	Et_3SiH; -78^{o}C to 0^{o}C, 30 min.	(6)	96%
3	(5)	TMSOTf	Et_3SiH; -78^{o}C, 1 hr.	(6)	98%
4	(5)	CH_3CO_2H	Et_3SiH; rt 2 days	(6)	0%
5	(5)	TMSOTf	Ph_3SiH; -78^{o}C, 1 hr.	(6)	74%
6	(5)	TFA	Ph_3SiH; -78^{o}C, 1 hr.	(6)	54%
7	(5)	TFA-d_1	Et_3SiH; -78^{o}C, 1 hr.; 0^{o}c, 1 hr.	(7)	95%
8	(8)	TMSOTf	Et_3SiH; -78^{o}C, 1 hr.	(9)	87%
9	(8)	TFA	Et_3SiH; -78^{o}C, 1 hr.; 0^{o}C, 1.5 hrs.	(9)	24%
10	(8)	$BF_3.OEt_2$	Et_3SiH; -78^{o}C, 1 hr.; rt, 22 hrs.	(9)	15%
11	(10)	TMSOTf	Et_3SiH; -78^{o}C, 1 hr.	(12)	61%
12	(11)	TFA	Et_3SiH; -78^{o}C, 1 hr.	(13)	64%
13	(14)	TMSOTf	Et_3SiH; -78^{o}C, 1 hr.	(15)	80%
14	(14)	TFA	Et_3SiH; -78^{o}C, 1 hr.; 0^{o}c, 1 hr.	(15)	83%
15	(16)	TMSOTf	Et_3SiH; -78^{o}C, 1.5 hrs.	(17)	41%*
16	(19)	TMSOTf	E_3SiH; -78^{o}C, 1 hr.	(21)	72%
17	(20)	$BF_3.OEt_2$	Et_3SiH; -78^{o}C, 1 hr.; rt 4 days	(22)	42%
18	(20)	TMSOTf	Et_3SiH; -78^{o}C, 1 hr.; 0^{o}C, 5 hrs.; rt, 4 days	(22)	24%
19	(20)	TFA	Et_3SiH; -78^{o}C, 1 hr.; 0^{o}C, 1 hr; rt, 4 hrs.	(22)	24%

(*Together with 0.5% *cis*-isomer (**18**))

Table

In conclusion, we have developed a general method for the preparation of functionalised β-stannyl propionates from vinyl stannanes. It should also be noted that this procedure is readily amenable to scale-up; for example reduction of the stannane (5) on a 5g (15 mmol.) scale was accomplished with no diminution in yield (*ca* 90 %) after a simple aqueous work-up and silica gel filtration.

Stannanes such as (4) are potentially useful synthetic intermediates, serving as a source of functionalised homoenolates[15] whose chemistry is now under active scrutiny[16].

General Experimental Procedure

The following experimental procedure is representative:-to a solution of the vinyl stannane (5) (0.2554 g, 0.61 mmol) in dry dichloromethane (20 ml) at -78°C under an atmosphere of dry nitrogen was added TFA (0.14 g, 0.1 ml, 1.225 mmol) followed by triethylsilane (0.71g, 0.98 ml, 6.1 mmol). After one hour at -78°C and 30 mins. at 0°C, the reaction mixture was allowed to warm up to room temperature and quenched by the addition of excess saturated aqueous sodium hydrogencarbonate solution. The organic layer was separated and the aqueous layer was extracted (2x20 ml CH_2Cl_2). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. "Flash" chromatography of the crude product afforded the stannane (6) as a clear colourless oil.; yield 0.2458g (96%).

Acknowledgements

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