Unusual Addition Reactions of Alkoxymethyl Substituted Allylstannanes to a Carbonyl Compound. Complete Product Control by the Alkoxy Group Regardless of Original Regio- and Stereo-chemistry

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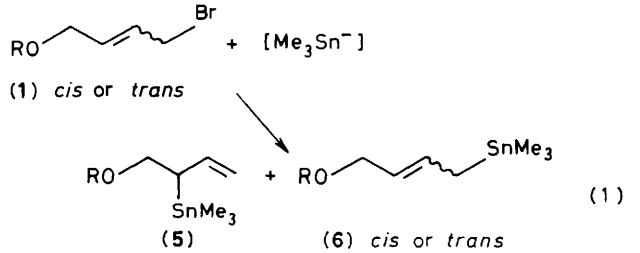
Alkoxymethyl substituted allylstannanes have been prepared and their Lewis acid mediated allylation of a carbonyl compound results in the formation of the corresponding *cis*-4-alkoxymethylbut-3-en-1-ol regardless of the regio-and stereo-chemistry of the original allylstannanes.

Control of the regioselectivity of allylic organometallic compounds is one of the major problems in organic chemistry.[1] High nucleophilicity at the γ position of allyl-silane and -stannane has been established to be due to σ–π conjugation. Regioselective allylation by these compounds has been extensively used in organic synthesis.[2,3] Allylsilanes in Lewis acid mediated reactions show γ selectivity without exception,[4] while the stannyl derivatives have been reported to show α selectivity in some cases.[5] We prepared allylstannanes substituted with alkoxymethyl groups and achieved an unusual type of nucleophilic addition to a carbonyl group in the presence of $SnCl_4$.

The allylstannanes were prepared by the coupling reaction of (**2**),[6] (**3**), or (**4**)[7,8] with *cis*- or *trans*-4-alkoxybut-2-enyl bromide† (**1**) at −30 [(**2**), (**3**)] or −78 °C [(**4**)], [equation (1)].



(1)

$[Me_3Sn^-] = [(Me_3Sn)_2Cu]Li$ (**2**)

$[Me_3SnCuC{\equiv}CC(Me)_2OMe]Li$ (**3**)

Me_3SnLi or Me_3SnNa (**4**)

† Each 4-alkoxybut-2-enyl bromide with defined stereochemistry was prepared separately in >96% purity from 2-alkoxy- or 2-phenyl-4,5,6,7-tetrahydro-1,3-dioxepine.

The results are summarized in Table 1. The stereochemistry of the allyl bromides was retained, while the regioselectivity of the reaction (α *vs.* γ) varied with both the stannyl reagent used and the stereochemistry of the bromide. The reaction of Me_3SnLi (or Na) (**4**) with (**1**) proceeded *via* an S_N2 process only, while the stannylcuprates, (**2**) and (**3**), gave both S_N2 and S_N2' adducts. The regioisomers were separated and purified

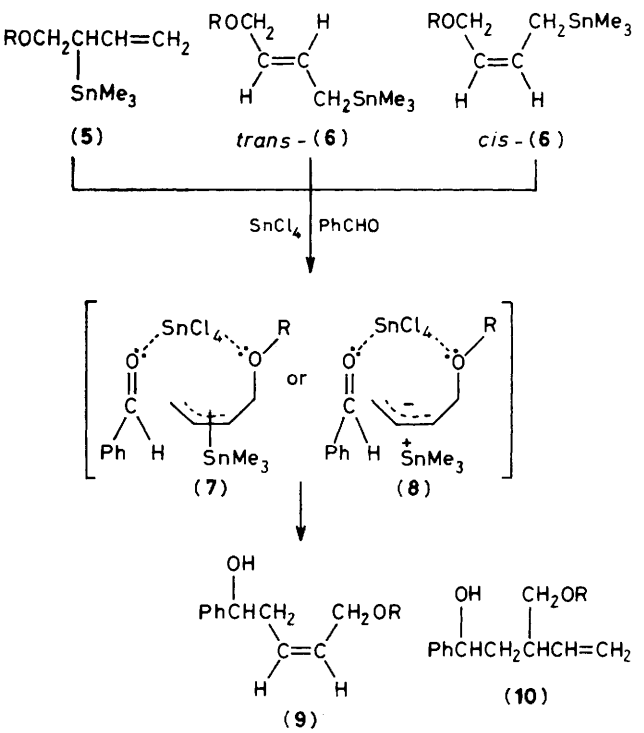


Table 1

R	Halide (1) Stereochemistry[a]	$[Me_3Sn^-]$[b]	Allylstannane isomeric ratio[c] (5)	*cis*-(6)	*trans*-(6)	Isolated yield, %[d]
Et	*cis*	(3)	18	82	0	47
"	*trans*	(3)	65	0	35	72
Pr^i	*cis*	(3)	45	55	0	70
$PhCH_2$	*cis*	(2)	67	33	0	98
"	*cis*	(3)	10	90	0	42
"	*cis*	(4)	0	100	0	42
"	*trans*	(2)	67	0	33	61
"	*trans*	(3)	67	0	33	24
"	*trans*	(4)	0	0	100	28
Ph(Me)CH	*cis*	(3)	10	90	0	75

[a] Isomeric purity >99%. [b] Reaction conditions: (2) and (3), −30 °C in tetrahydrofuran (THF); (4), −78 °C in THF or triglyme. [c] Determined by ^1H n.m.r. spectroscopy. [d] Mixture of regioisomers after distillation.

by column chromatography on silica gel (hexane–diethyl ether eluant) without extensive decomposition.‡

Nucleophilic addition of the allylstannane (**5**) (R = Et) to benzaldehyde in the presence of $SnCl_4$ at −78 °C in CH_2Cl_2 afforded the adduct (**9**) (R = Et) in 78% isolated yield with high stereoselectivity (*cis*: *trans* 97 : 3). Interestingly, *cis*-(**6**) (R = Et) gave adduct (**9**) only in 67% isolated yield with preservation of *cis* stereochemistry (>99%) on reaction with PhCHO under similar conditions. The adduct (**10**) was not detected in the reaction mixture. More interestingly, *trans*-(**6**) (R = Et) gave the same *cis* adduct (**9**) with complete inversion of stereochemistry (*cis*: *trans* 97 : 3) in 80% yield. A similar result was observed in the reaction of the benzyloxy derivatives, (**5**) and (**6**) (R = CH_2Ph), which afforded the single adduct (**9**) (R = CH_2Ph) in 56—67% isolated yield (*cis*:*trans* > 98 : 2) regardless of the regio- and stereo-chemistry of (**5**) and (**6**). Mixtures of allylstannanes [*e.g.* (**5**) + *cis*- or *trans*-(**6**), or *cis*-(**6**) + *trans*-(**6**)] also confirmed the above results by giving the *cis* adduct (**9**) only. This product specificity was also observed in reactions with other alkoxymethyl substituted allylstannanes [R = Pr^i, Ph(Me)CH], and it was concluded to be general for these stannyl compounds.

This uniformity can not be explained in terms of σ–π conjugation. It may be understood by considering a cyclic transition state consisting of the dibasic Lewis acid $SnCl_4$, the aldehyde, and the allylstannane. In this transition state allylic rearrangement [*e.g.* (**7**)] or dissociation of the trimethylstannyl group [*e.g.* (**8**)] may occur preferentially. This argument is also supported by the fact that monobasic Lewis acids, *e.g.* $BF_3{\cdot}OEt_2$, $AlCl_3$,§ were ineffective in this reaction and only caused decomposition of the allylstannanes.

‡ Generally allylstannanes decompose easily on silica gel.

§ Unsubstituted allylstannanes provided allylated products in good yields in the presence of these Lewis acids.

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