Organometallic High Pressure Reactions. Allylation of Aldehydes with Allylic Stannanes under Mild Conditions

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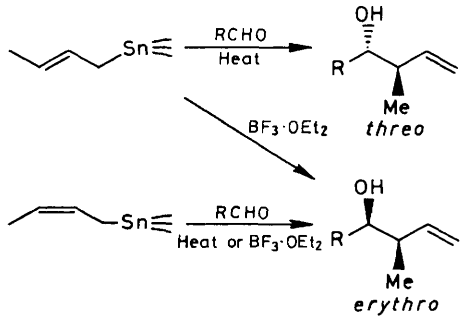
Allylation of aldehydes with allylic stannanes takes place at room temperature under neutral conditions by using a high-pressure technique.

Allylation of aldehydes with allylic organometallic compounds has recently received wide attention as a basic synthetic method for control of acyclic stereochemistry.[1] Among many allylic organometallic reactions, the Lewis acid-mediated reaction of allylic stannanes and silanes is noteworthy; *erythro*-homoallyl alcohols are obtained predominantly regardless of the geometry of the but-2-enyl unit (Scheme 1).[2] In marked contrast, however, the stereochemistry in thermal reactions of but-2-enyl stannane derivatives generally depends upon the geometry of the but-2-enyl unit[3] as observed in ordinary allylic organometallic reactions; the *E*-isomer produces *threo*-alcohols while the *Z*-isomer affords *erythro*-alcohols.

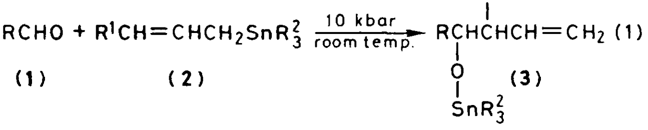


Scheme 1. Allylation with but-2-enylstannanes.

To help clarify the factors responsible for this striking stereochemical difference and to develop a new mild allylating procedure, we have examined the reaction of allylic trialkylstannanes with aldehydes under high pressure (10 kbar, 1 GPa).[4]

To our surprise, the allylation occurred at room temperature under neutral conditions [reaction (1)], by far the mildest conditions reported to date for this kind of reaction. The results are summarized in Table 1.

After the period† indicated in Table 1, the pressure was released and the solvent removed *in vacuo*. The products were directly analysed by ^{1}H n.m.r. spectroscopy. The reaction was clean and polymerization products were not detected. When the reaction was incomplete (entries 2, 4, 5, 7, and 8), the aldehyde and allylic stannane were recovered without change. The adducts (**3**) were easily hydrolysed with water to give the corresponding homoallyl alcohol. ^{1}H N.m.r. analysis revealed that the *threo*-isomer is formed predominantly from the *trans*-but-2-enylstannane (entries 2 and 4). This indicates that the



$$\underset{(1)}{\mathrm{RCHO}} + \underset{(2)}{\mathrm{R^1CH{=}CHCH_2SnR^2_3}} \xrightarrow[\text{room temp.}]{\text{10 kbar}} \underset{\underset{\mathrm{SnR^2_3}}{\mathrm{O}}}{\mathrm{RCH}}\overset{\mathrm{R^1}}{\mathrm{CH}}\mathrm{CH{=}CH_2}\ (3) \quad (1)$$

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† Conditions are not optimized. Allylation with allylic silanes did not occur under these conditions.

Table 1. Allylation of aldehydes under high pressure.[a]

Entry	R in **(1)**	Stannane R^1	**(2)** R^2	Time/ day	Solvent	% Yield of **(3)**[b]
1	Ph	H	Me	5	Et_2O	*ca.* 100
2	Ph	Me	Bu^n	3	Et_2O	41[c,d]
3	p-MeC_6H_4	H	Me	7	Et_2O	*ca.* 100
4	p-MeC_6H_4	Me	Bu^n	7	Et_2O	17[c,e]
5	p-$MeOC_6H_4$	H	Me	6	CH_2Cl_2	40
6	p-$O_2NC_6H_4$	H	Me	6	CH_2Cl_2	*ca.* 100
7	PhCH=CH (*E*)	H	Me	6	CH_2Cl_2	83
8	Pr^n	H	Me	7	CH_2Cl_2	70

[a] In a Teflon capsule (1.5 ml capacity) were placed the aldehyde (1 mmol), the allylic stannane (1 mmol), and solvent (*ca.* 1 ml). High pressure (10 kbar) experiments were performed in a stainless steel die and compressed at room temperature *via* a piston. [b] By ^1H n.m.r. spectroscopy. [c] By ^1H n.m.r. spectroscopy of the hydrolysis product. [d] *erythro*:*threo* = 35:65. [e] *erythro*:*threo* = 20:80.

reaction of allylic stannanes with aldehydes proceeds essentially *via* a six-membered cyclic transition state owing to the affinity of the Sn atom for the carbonyl oxygen atom, as suggested previously.[3] Lewis acids co-ordinate to the oxygen atom preventing the co-ordination of the Sn atom, resulting in a synthetically useful stereochemical convergence.[2] In addition to this mechanistic interest, the present finding provides a new, mild, procedure for allylation of aldehydes which may be useful for the synthesis of complex molecules.

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