Synthesis and Reactions of an Allylic Stannane

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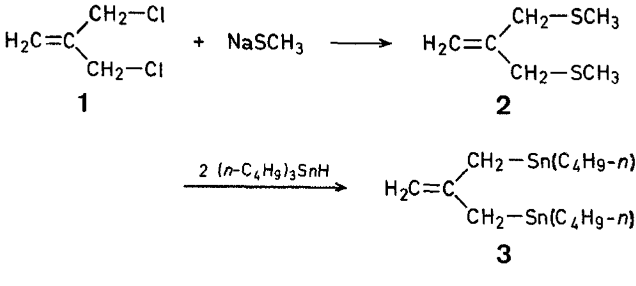
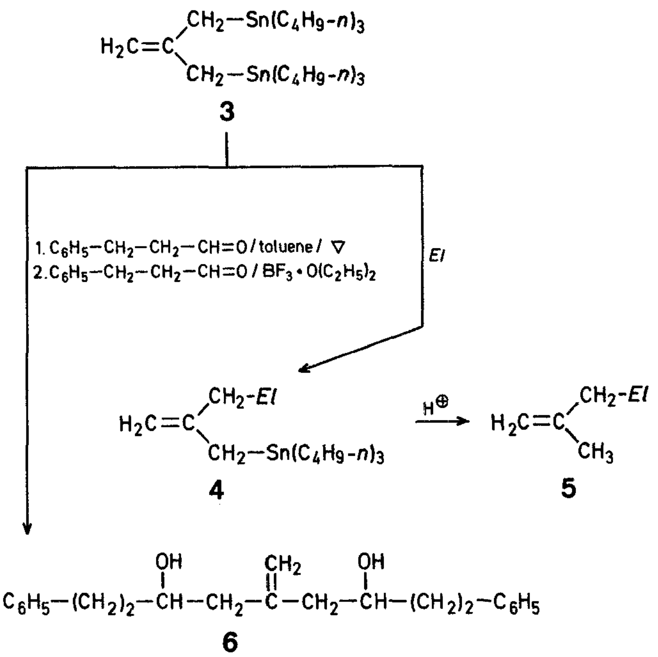
Allylstannanes as well as allylsilanes are important allylating agents for various electrophiles, since they react with electrophiles in a highly regiospecific manner[2]. Allylstannanes themselves, however, are not very reactive and require a certain activation process. For example, allylstannanes react with aldehydes only under severe conditions[3], or in the presence of a Lewis acid catalyst[4].

We report here a new type of activation of allylstannanes. Our idea is based upon the assumption that bis[organostannyl] groups might have a profound effect on the activation of the allylic double bond. 1,3-Bis[tributylstannyl]-2-methylenepropane (**3**) was succesfully prepared in 75% yield by the stannolysis of 1,3-bis[methylthiomethyl]-2-methylenepropane (**2**) with tri-*n*-butyltin hydride[5]. Compound **2** was obtained by the reaction of 1,3-dichloro-2-methylenepropane (**1**) with sodium methylmercaptide. Recently, the preparation of similar allylstannanes by the reaction of 1,3-dichloro-2-methylenepropane with stannyllithium has been reported[6].

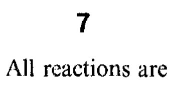


The allylstannane **3** is found to be highly reactive towards several electrophiles such as aldehydes, acid chlorides, and π-allylpalladium complexes; the reaction proceeding in a completely selective manner. That is, only one stannyl group is substituted by the electrophiles to give **4**, and the second stannyl group remains intact under the conditions used. The destannylation to the final products is achieved by hydrochloric acid **5** (Table).



Normal allylstannes require high temperatures (> 200 °C) or reflux conditions e.g. in tetrahydrofuran, for the reaction with aldehydes or the π-allylpalladium complex, respectively. With the allylstannane **3**, the reaction with electrophiles could be carried out at lower temperatures (Table). In the case of acid chlorides (Table), isomerization of the double bond leading to α,β-enones was observed during acid treatment. Chemoselective methallylation of aldehydes or acid chlorides in the presence of ketone functionality can be achieved, since **3** scarcely react with ketones under similar conditions. The stepwise double alkylation is also promising. Thus, first a thermal reaction followed by the Lewis acid catalyzed reaction afforded the dialkylated compound **6** in 36% overall yield.

In summary, the present reaction offers an alternative activation mode for allylstannanes, and the compound **3** is useful as a isobutene dianion synthon 7.



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All reactions are carried out under nitrogen.

1,3-Bis[methylthio]-2-methylene propane(2):

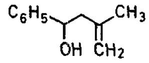
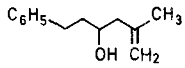
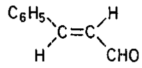
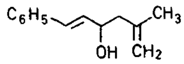
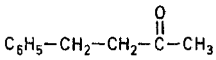
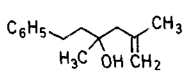
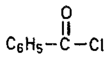
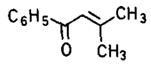
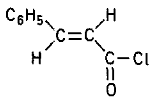
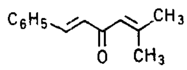
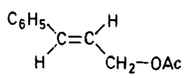
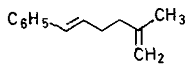
A mixture of 1,3-dichloro-2-methylenepropane (**1**; 5 g, 40 mmol), 15% aqueous sodium methylmercaptide solution (50 ml, 107 mmol), and a catalytic amount of cetyltributylphosphonium bromide is stirred at room temperature for 6 h. To the resultant mixture is added ether (50 ml), then the ether layer is separated, washed with water (2 × 20 ml), dried with magnesium sulfate, and evaporated. The crude product **2** is purified by distillation; yield: 5.7 g (96%); b.p. 80–81 °C/6 torr.

$C_6H_{12}S_2$	calc.	C 48.60	H 8.16
(148.3)	found	48.45	8.24

I.R. (Film): $\nu = 1600\ cm^{-1}$. (C=C).

^1H-N.M.R. ($CDCl_3$): $\delta = 2.0$ (s, 6H); 3.25 (s, 4H); 4.95 ppm (s, 2H).

Table. Reactions of Electrophiles with Allylstannane

Electrophile	Product		Reaction Conditions solvent/Temp./Time	Yield[a] [%]	Molecular formula[b]	^{1}H-N.M.R. (CDCl$_3$) δ[ppm]
C_6H_5-CHO	**5a**		toluene/reflux/2 h	83	–[c]	see experimental
$C_6H_5-CH_2-CH_2-CHO$	**5b**		toluene/reflux/2 h	88	$C_{13}H_{18}O$ (190.3)	1.6–2.25 (m, 8 H); 2.55–3.0 (m, 2H); 3.7 (m, 1H); 4.85 (m, 2H); 7.2 (s, 5H)
	**5c**		toluene/reflux/2 h	82	$C_{13}H_{16}O$ (188.3)	1.8 (s, 3H); 1.9 (d, 1H, $J = 3$ Hz); 2.4 (d, 2H, $J = 7$ Hz); 4.45 (m, 1H); 4.90 (br. s, 2H); 6.3 (dd, 1H, $J = 16$ Hz, 5 Hz); 6.65 (d, 1H, $J = 16$ Hz); 7.3 (m, 5H)
 $C_6H_5-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	**5d**		toluene/reflux/11 h	6	$C_{14}H_{20}O$ (204.3)	1.25 (s, 3H); 1.7 (s, 1H); 1.7–2.0 (m, 5H); 2.25 (s, 2H); 2.5–2.9 (m, 2H); 4.8 (s, 1H); 4.95 (s, 1H); 7.2 (s, 5H)
 $C_6H_5-\overset{O}{\overset{\|}{C}}-Cl$	**5e**		toluene/reflux/2 h	54	–[c]	2.0 (s, 3H); 2.25 (s, 3H); 6.75 (br. s, 1H); 7.2–8.2 (m, 5H)
	**5f**		toluene/reflux/2 h	59	–[c]	1.95 (s, 3H); 2.2 (s, 3H); 6.3 (br. s, 1H); 6.7 (d, 1H, $J = 7$ Hz); 7.1–8.0 (m, 6H)
	**5g**		THF/r.t./19 h[d]	45	$C_{13}H_{16}$ (172.3)	see experimental

[a] Yield of product isolated by column chromatography.
[b] Satisfactory microanalyses obtained: C ± 0.28, H ± 0.17.
[c] Structure confirmed by comparison of spectral data with those reported (**5a**[8], **5e**[9], **5f**[10]).
[d] 10% Pd[P(C_6H_5)$_3$]$_4$ used as catalyst.

1,3-Bis[tributylstannyl]-2-methylenepropane (3):

A mixture of 1,3-bis[methylthio]-2-methylenepropane (**2**; 0.6 g, 4.05 mmol), tributyltin hydride (2.84 g, 9.75 mmol), and a catalytic amount of azobisisobutyronitrile in dry benzene (15 ml) is heated under reflux for 2 h. Benzene is evaporated under reduced pressure and the residue is distilled to give allylstannane **3**; yield: 1.94 g (75%); b.p. 160–165 °C/0.04 torr (Kugelrohr distillation).

$C_{28}H_{60}Sn_2$	calc.	C 53.03	H 9.54
(634.2)	found	52.76	9.71

^{1}H-N.M.R. (CDCl$_3$): $\delta = 0.4$–2.2 (m, 58H); 4.2 ppm (t, 2H, $J = 9$ Hz).

1-Phenyl-3-methyl-3-butene-1-ol (5a); Typical Procedure:

A mixture of 1,3-bis[tributylstannyl]-2-methylenepropane (**3**; 1.6 g, 1.67 mmol) and benzaldehyde (0.15 g, 1.42 mmol) in dry toluene (2 ml) is heated under reflux for 3 h. To the resultant mixture are added at room temperature aqueous 1 normal hydrochloric acid (5 ml) and ether (5 ml) with stirring for 2 h. The ether layer is separated, washed with aqueous sodium hydrogen carbonate solution (2 × 10 ml), dried with magnesium sulfate, and evaporated. The crude product is purified by column chromatography on silica gel, eluting with *n*-hexane and subsequently with chloroform; yield: 0.19 g (83%). The structure of **5a** is confirmed by comparison of the spectral data with those reported[8].

I.R. (film): $\nu = 3400$ (OH); 1650 cm^{-1}. (C=C).

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.8$ (s, 3H); 2.3 (1H); 2.4 (d, 2H, $J = 7$ Hz); 4.6–5.0 (m, 3H); 7.3 ppm (s, 5H).

5-Methyl-1-phenyl-1,5-hexadiene (5g):

A mixture of 1,3-bis[tributylstannyl]-2-methylenepropane (**3**; 1.2 g, 1.89 mmol), cinnamyl acetate (0.139 g, 0.79 mmol), and tetrakis [triphenylphosphine]palladium (0.092 g, 0.08 mmol) in dry tetrahydrofuran (3 ml) is stirred for 19 h at room temperature. Similar work-up as described for compound **5a** gives the product **5g**; yield: 0.122 g (45%).

$C_{13}H_{16}$	calc.	C 90.64	H 9.36
(172.3)	found	90.52	9.41

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.8$ (s, 3H); 2.0–2.6 (m, 4H); 4.75 (s, 2H); 6.15–6.45 (m, 2H); 7.3 ppm (m, 5H).

1,1-Bis[4-phenyl-2-butanol-1-yl]ethene (6):

A mixture of 1,3-bis[tributylstannyl]-2-methylenepropane (**3**; 0.6 g, 0.95 mmol), and 3-phenylpropionaldehyde (0.13 g, 0.97 mmol) in dry toluene (2 ml) is heated under reflux for 3 h. To the resultant mixture is added 3-phenylpropionaldehyde (0.13 g, 0.97 mmol) in dry dichloromethane (3 ml). After cooling at −65 °C, boron trifluoride etherate (0.35 ml, 2.85 mmol) is added to the mixture followed by stirring at room temperature for 1 h. Water (3 ml) and ether (10 ml) are added to the solution, and then the ether layer is separated, dried with magnesium sulfate, and evaporated. The crude product is purified by column chromatography on silica gel eluting with chloroform; yield: 0.11 g (36%).

$C_{22}H_{28}O_2$	calc.	C 81.44	H 8.70
(324.5)	found	81.66	8.83

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.5$–3.0 (m, 14H); 3.5–4.0 (m, 2H); 4.95 (s, 2H); 7.2 ppm (s, 10H).

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