Z-Stereoconvergent Synthesis of Homoallylic Alcohols by Addition of $Bu_2ClSnCH(CH_3)CH=CH_2$ and α-β-Unsaturated Aldehydes

ANDREA BOARETTO, DANIELE MARTON , GIUSEPPE TAGLIAVINI*

Istituto di Chimica Analitica, Università di Padova, Via Marzolo 1, 35100 Padua, Italy

and ALESSANDRO GAMBARO

Istituto di Chimica Fisica, Università di Padova, Via Loredan 2, 35100 Padua, Italy

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Homoallylic alcohols, $RCH(OH)CH_2CH=CHCH_3$, have been synthetized wholly in the Z-isomeric form by reacting $Bu_2ClSnCH(CH_3)CH=CH_2$ with α-β-unsaturated aldehydes, RCHO ($R=CH_2=CH-$, $CH_2=CH(CH_3)-$, $(E)CH_3CH=CH-$, and $(E)C_3H_7-CH=CH-$).

The addition of substituted allylic organometallic compounds to aldehydes provides a useful route to the stereoselective formation of new C–C bonds [1]. Recently chloroallyltins such as $Bu_{3-n}SnCl_n$-$CH_2CH=CH_2$ and $Bu_{3-n}SnCl_nCH_2CH=CHCH_3$ (n = 1, 2, 3) have been successfully used in addition reactions with many carbonyl compounds to give stereocontrolled synthesis of homoallylic alcohols [2] and heterocyclic halo-tetrahydropyrans [3]. Furthermore $Bu_2SnClCH(CH_3)CH=CH_2$ (I), which can be generated *in situ* by redistribution of $(E/Z)Bu_3SnCH_2$-$CH=CHCH_3$ and Bu_2SnCl_2, has been shown to react readily with aldehydes in the absence of solvents to give linear alcohols of the type $RCH(OH)CH_2CH=CHCH_3$ wholly in the Z-configuration [4].

We now report reactions between (I) and α,β-unsaturated aldehydes, RCHO ($R=CH_2=CH-$, $CH_2=C(CH_3)-$, $(E)CH_3CH=CH-$, and $(E)C_3H_7CH=CH-$) which lead to linear homoallylic alcohols wholly in the Z-configuration. The results, together with ^{13}C nmr chemical shifts and relevant IR frequencies, are summarized in Table I.

Manipulation of the reactants is very easy since all reactions are carried out at room temperature without solvents or an inert atmosphere. The general procedure adopted was as follows: equimolar amounts (25 mmol) of $(E/Z)Bu_3SnCH_2CH=CHCH_3$ (E/Z typically 3/1) and RCHO were mixed and the mixture added as quickly as possible with stirring to solid Bu_2SnCl_2 in the molar ratio $Bu_3SnCH_2CH=CHCH_3/Bu_2SnCl_2=1/1.5$. The Bu_2SnCl_2 dissolves almost at once and the progress of the reaction was then monitored by IR-spectroscopy: complete disappearance of the carbonyl stretching band at 1750–1700 cm^{-1} marked the end of the reaction, which was usually reached after about 20 h. Aqueous NH_4Cl was then added and the carbinol and organotin compounds extracted with ether. Subsequently the carbinol was separated by distillation in yields of 80–90%. In all cases only Z-crotyl carbinols were obtained, together with small amounts of branched methylallyl carbinols, $RCH(OH)CH(CH_3)CH=CH_2$ (Table I), produced by partial isomerization of (I).

Assignment of the *Z* configuration was made by IR spectroscopy (compare data in Table I with lit. data [5]) and confirmed by ^{13}C NMR spectra.

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*Author to whom correspondence should be addressed.

TABLE I. Results for the addition reactions. ^{13}C-NMR chemical shifts[a] and relevant IR data of the prepared compound.

Alcohol	Yield (%)	Composition of the product mixture	
		Z-linear %	Branched %
1 2 3 4 5 6 7 $CH_3-CH=CH-CH_2-CH(OH)-CH=CH_2$	82	98	2
1 2 3 4 5 6 6′ 7 $CH_3-CH=CH-CH_2-CH(OH)-C(CH_3)=CH_2$	90	98	2
1 2 3 4 5 6 7 8 $CH_3-CH=CH-CH_2-CH(OH)-CH=CH-CH_3$	83	91	9
1 2 3 4 5 6 7 8 9 10 $CH_3-CH=CH-CH_2-CH(OH)-CH=CH-CH_2-CH_2-CH_3$	85	90	10

[a] Values from internal Me_4Si. [b] Deformation out of plane of the (Z)=CH.

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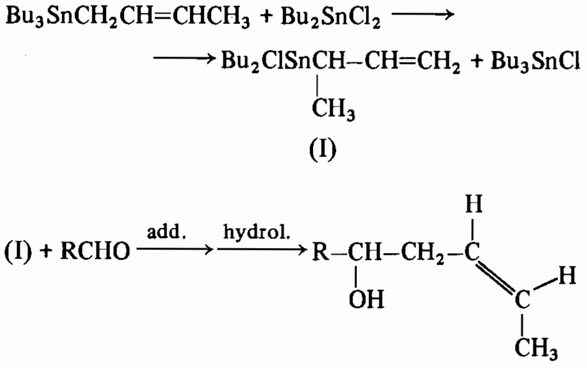
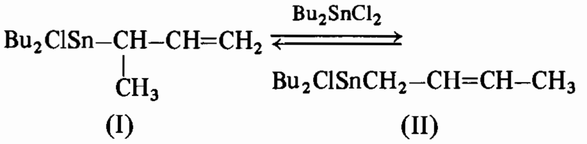
The reaction scheme may be represented as:



$$Bu_3SnCH_2CH=CHCH_3 + Bu_2SnCl_2 \longrightarrow \underset{\substack{CH_3\\(I)}}{Bu_2ClSnCH}-CH=CH_2 + Bu_3SnCl$$

It must be emphasized that both these reactions are characterized by complete allylic rearrangements. These results, together with previous findings on the redistribution reactions of allyltin substrates [6], show that reactions of α-methylally substrates are kinetically controlled so as to yield almost exclusively Z-configuration products. The recovery of small amounts of branched alcohols depends upon the metallotropic rearrangements [6, 7]:



$$\underset{\substack{CH_3\\(I)}}{Bu_2ClSn-CH}-CH=CH_2 \overset{Bu_2SnCl_2}{\rightleftharpoons} \underset{(II)}{Bu_2ClSnCH_2-CH=CH-CH_3}$$

and the relative rates of reaction of RCHO with the two isomers (I) and (II). When reaction with (II) is much slower than with (I) the recovered alcohol is mainly *Z*-linear, as in Table I.

A significant finding, previously reported, is that $(CH_3)_3CCHO$ does not react with (II) [3], and gives only *Z*-linear homoallylic alcohol as product [4]. The formation of *Z*-linear homoallylic alcohols which retain the original R group in the *E* configuration ((*E*)$CH_3CH=CH$– and (*E*)$C_3H_7CH=CH$–) shows that conjugated addition is precluded.

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Chemical Shifts (p.p.m.)											IR data (cm^{-1})			
C_1	C_2	C_3	C_4	C_5	C_6	$C_{6'}$	C_7	C_8	C_9	C_{10}	$\tilde{\nu}_{OH}$	$\tilde{\nu}_{C(2)=C(3)}$	$\tilde{\nu}_{C(6)=C(7)}$	$\delta_{=CH}^{b}$
13.0	125.7	126.5	35.1	72.6	141.3	–	114.2	–	–	–	3370 s	1651 m	1636m	708 m
13.0	125.4	127.2	33.3	75.6	147.8	17.7	111.0	–	–	–	3370 s	1649 m	1644 m	691m
13.1	127.0	127.0	35.5	72.5	134.2	–	125.5	17.7	–	–	3552 s	1653 m	1678 m	704 m
13.1	127.1	127.1	35.7	72.4	134.1	–	130.4	34.8	22.8	13.8	3406 s	1653 m	1684 m	704 m