Allylstannation as a Route to 4-Halo-2,6-disubstituted Tetrahydropyrans $CH(X)–CH_2–(CH(C_2H_5)–O–CH(C_2H_5)–CH_2$ (X = Cl, Br)

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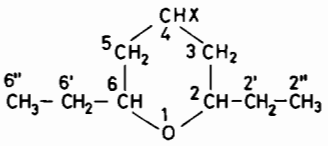
The most important general methods for synthesis of six-membered heterocycles are still those based on cyclization of diols and haloalcohols. Moreover, some modifications of the Prins reaction [1], in which 1-olefins are condensed with aldehydes and hydrogen halides, lead to 4-halo-3-alkyl-tetrahydropyrans [2].

During our investigations on allylstannation [3], we discovered that tetrahydropyrans of the formula



(X = Cl, Br) (1)

can be easily synthesized by working-up the system $Bu_3SnCH_2CH=CH_2/C_2H_5CHO$ in the presence of SnX_4 (X = Cl, Br). The use of these substrates, together with others such as $BuCl_2SnCH_2CH=CHCH_3$/RCHO and $Bu_3SnCH_2CH=CHCH_3$/RCHO/$BuSnCl_3$, promises to be a general method in synthesizing this class of compounds [4].

The synthesis was performed by adding, at –15 °C under stirring, 30 mmol of SnX_4 (X = Cl, Br) to a mixture of 30 mmol of $Bu_3SnCH_2–CH=CH_2$ and 66 mmol of C_2H_5CHO. Then the system was allowed to react for 1 hr at room temperature. After hydrolysis with Na_2CO_3 2 *M* (15 ml) the reaction products were extracted with ethyl ether. The solvent was taken off by distillation and the residue analyzed by gas chromatography. In such a way compounds (1) were obtained: X = Cl, 90% yield, b.p. 56–57 °C/3 mm Hg; X = Br, 85% yield, b.p. 75–77 °C/5 mm Hg. Their identification was carried out by ^{13}C n.m.r. spectroscopy and mass spectra: the ^{13}C chemical shifts together with relevant i.r. stretching frequencies and gas-chromatographic data are listed in Table I.

The reaction path may be represented by the following steps:

$$Bu_3SnCH_2CH=CH_2 + SnX_4 \longrightarrow Bu_3SnX + CH_2=CHCH_2SnX_3 \quad (a)$$

(2)

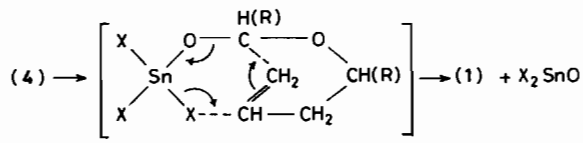
$$(2) + RCHO \longrightarrow X_3SN–O–CH(R)–CH_2CH=CH_2 \quad (b)$$

(3)

$$(3) + RCHO \longrightarrow X_3Sn–O–CH(R)–O–CH(R)–CH_2CH=CH_2 \quad (c)$$

(4)

Adduct (4) collapses into compound (1) through an intramolecular rearrangement:



The above scheme takes into account the ease of the insertion of aldehydes into the SnC bond [3]

TABLE I. ^{13}C N.m.r. Shifts[a], Relevant I.r. and Gas-chromatographic Data of the Prepared Compounds.

Compound (1) X	p.p.m. carbon atoms[b]					$\bar{\nu}_{C-X}$ (cm^{-1})		g.l.p.c. retention times[c]
	2,6	2', 6'	2", 6"	3, 5	4	equatorial	axial	
Cl	78.0	29.2	9.9	42.8	56.1	760	580	5'6"
Br	78.5	28.9	9.9	43.4	47.0	705	560	7'18"

[a]Values from internal Me_4Si. [b]See formula (1). [c]Column (2 m, 1/8 inch) filled with SE30; t_c = 150 °C, t_d = 270 °C, t_i = 250 °C; nitrogen flow rate 20 ml/min.

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in haloallytin substrates (step b), as well as the subsequent insertion of aldehydes into a Sn–O bond [5] (step c).

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