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COBALT MEDIATED REGIOREVERSED ADDITION OF But-2-ENYLTRIBUTYLSTANNANE TO ALDEHYDES

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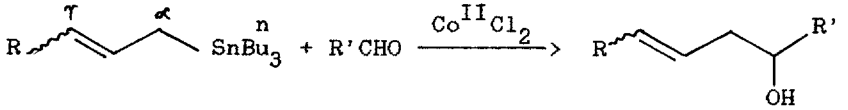
Summary. The addition of allyltributylstannane (**1**) and but-2-enyltributylstannane (**2**) to aldehydes (**3**) in presence of cobalt(II) chloride proceeds in a regioreversed manner as indicated by the exclusive formation of α-adducts (**5**) from (**2**) in good yields.

The addition of allylicstannanes to carbonyl compounds is now a very well established carbon-carbon[1] bond-forming reaction. These reactions require a Lewis acid (e.g. $TiCl_4$, $BF_3.Et_2O$, $SnCl_4$ etc.) which presumably activates the carbonyl group toward nucleophilic attack by the allylicstannanes. However, a recent report has proved[2] the earlier speculation[3] by demonstrating that Lewis acids like $SnCl_4$ and $BF_3.Et_2O$ are also capable of undergoing a ligand exchange with allylicstannanes prior to the addition of aldehydes. Yamamoto et al. have shown the possibility of a transmetallation of allylicstannanes with Lewis acid in aluminium chloride and propan-2-ol mediated regioreversed addiion of aldehydes. The later finding is quite useful for gaining access to α-adduct from substituted allylicstannanes.

We now report that cobalt(II) chloride can also promote the regioreversed addition of allyltributylstannane (**1**) and but-2-enyltributylstannane (**2**) to a variety of aldehydes in good yields. Typically, aldehyde (3 mmol) and allyltributylstannane (3 mmol) were added to a solution of dry cobalt(II) chloride (3 mmol) in dry acetonitrile (20 mL) and the resulting mixture was stirred under nitrogen at room temperature for 12 hours. The reaction mixture was poured into excess of ether (100 ml) and the resulting mixture washed successively with saturated solution of sodium bicarbonate and water. Drying ($MgSO_4$) and evaporation of solvent yielded an oil which on purification by column chromatography (SiO_2) gave homoallylic alcohols. The reaction of allyltributylstannane (**1**) with aldehydes is very facile and a high yield of homoallylic alcohols are obtained (Table, entry 1-3). Interestingly, but-2-enyltributylstannane (**2**) gave the linear alcohol[4,5] (α-adduct) (**5**) exclusively (Table, entry 4-8). Yamammoto et al.[4] have been able to achieve this transformation although their procedure does not yield the α-adduct exclusively. The reaction with crotonaldehyde is quite interesting because we get only the α-adduct (Table, entry 7) whereas their procedure leads to the formation formation of γ-adduct exclusively. In contrast to the earlier findings the steric hinderance of the aldehyde (Table, entry 8) and the order of addition

TABLE. Reaction of Allylstannanes with Aldehydes in the Presence of Cobalt(II) Chloride



1, R = H; **2**, R = Me **3** **4**, R = H; **5**, R = Me

Entry	R	R'	Yield of (**4**) & (**5**) (%)[a,b]
1	H	C_6H_5	85
2		n-C_6H_{13}	84
3		Cyclo-C_6H_{11}	90 (45:55)[c]
4	CH_3	C_6H_5	54
5		n-C_6H_{13}	70
6		p-Br-C_6H_4	71
7		CH_3-CH=CH-	54
8		Cyclo-C_6H_{11}	74 (45:55)[c]

(a) Yield of the isolated product; (b) All the products were properly characterised by ^{1}H-NMR and IR spectroscopy and C, H analysis; (c) Ratio of cis:trans isomer.

of the reagents does not effect the regio-chemistry of these reactions. The diastereoselectivity with cyclohexanal was very poor, as a mixture of cis:trans (45:55) isomers were obtained (Table, entry 3 & 8) from allylicstannanes (**1**) and (**2**). The mechanism of this reaction is presently unclear, however following two observations are worth mentioning for understanding the role of cobalt(II) chloride in these reactions. (1) Allylicstannanes react with cobalt(II) chloride in the absence of aldehydes to yield a green solid which does not show the presence of any paramagnetic cobalt(II) species on an e.s.r. analysis. (2) The order of addition of the reactants in case of but-2-enyltributylstannane (**2**) did not alter the course of the reaction. This indicates that cobalt(II) chloride preferentially reacts with the allylic stannanes and does not behave as a typical Lewis acid. Regardless of the mechanistic detail, the cobalt(II) chloride mediated addition of (**2**) to aldehydes is a very efficient way to linear homoallylic alcohols.

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