Regioreversed Addition of But-2-enyltributylstannane to Aldehydes in the Presence of Aluminium Chloride–Propan-2-ol

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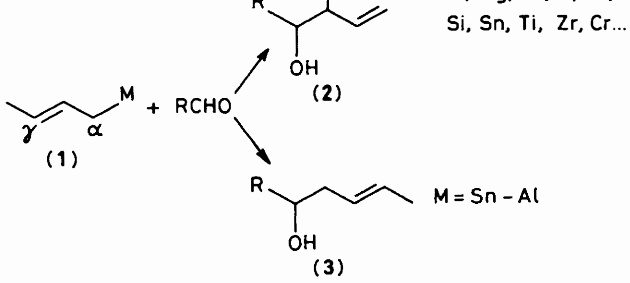
The reaction of but-2-enyltributylstannane with certain aldehydes in the presence of $\mathrm{AlCl_3}$–$\mathrm{Pr^iOH}$ produces the α-adduct (**3**) either predominantly or exclusively, while the reaction in the presence of ordinary Lewis acids, such as $\mathrm{TiCl_4}$, $\mathrm{SnCl_4}$, and $\mathrm{BF_3{\cdot}OEt_2}$, affords the γ-adduct (**2**) exclusively.

In general, the reaction of unhindered carbonyl compounds with the substituted allylic organometallic reagent (**1**) results in the γ-adduct (**2**) in which the allylic group is attached at the more highly substituted position.[1] It is now widely recognized that reactions of this type are an important tool for acyclic stereocontrol.[2] However, the regioreversed addition to unhindered carbonyl compounds to produce the linear adduct (**3**) is totally unprecedented despite its great potential importance.[3] We report that the reaction of but-2-enyltributylstannane (**1**, M = $\mathrm{SnBu_3}$) with certain aldehydes in the presence of $\mathrm{AlCl_3}$–$\mathrm{Pr^iOH}$ produces the α-adduct (**3**) either predominantly or exclusively. The results are summarized in Table 1.

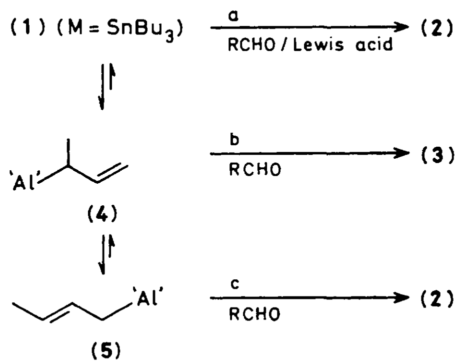


Linear aldehydes and benzaldehyde give the linear adducts (**3**) (entries 1—5), while the branched aldehyde (entry 7), crotonaldehyde (entry 8), and acetophenone give the branched adduct (**2**), exclusively. Isovaleraldehyde is a borderline case. These results indicate that the steric hindrance of the carbonyl group plays an important part in the regiochemistry of the addition. Another important factor is the order of addition of the reagents and the following procedure is representative.

Table 1. Reaction of (**1**) (M = $\mathrm{SnBu_3}$) with aldehydes in the presence of $\mathrm{AlCl_3}$–$\mathrm{Pr^iOH}$.

Entry	Aldehyde	Product ratio, %[a] (3)	Product ratio, %[a] (2)	*E/Z* Ratio[a,b]	Total yield, %[a]
1	PhCHO	83	17	90/10	80
2	EtCHO	98	2	90/10	67
3	$\mathrm{Pr^nCHO}$	95	5	85/15	72
4	$\mathrm{Bu^nCHO}$	90	10	87/13	73
5	n-$\mathrm{C_9H_{19}CHO}$	61	39	84/16	70
6	$\mathrm{Me_2CHCH_2CHO}$	58	42	87/13	68
7	$\mathrm{Me_2CHCHO}$	0	100	—	80
8	MeCH=CHCHO	0	100	—	80

[a] By g.l.c. analysis (CW-6000, column length 2 m). [b] *E/Z* Ratio of (**3**); for (**2**), a mixture of two diastereoisomers was obtained.



Scheme 1

In a dry 50 ml flask, maintained under a static pressure of N_2 and kept at −78 °C, were placed dry CH_2Cl_2 (4 ml) and $AlCl_3$–diethyl ether solution (2 M, 1 mmol). Propan-2-ol (1 mmol) was added and then but-2-enyltributylstannane (1 mmol). After 1—3 min, the aldehyde (1 mmol) was added and the stirring continued for 15 min at this temperature. The reaction was quenched at 0 °C, and analysed by g.l.c. If the aldehyde was added prior to the addition of but-2-enyltributylstannane, the ratio of (**2**) was increased and it became the major product in certain cases. Use of $AlCl_3$, instead of $AlCl_3$–Pr^iOH, produced (**2**) exclusively. Other Lewis acids, such as $TiCl_4$, $SnCl_4$, and $BF_3{\cdot}OEt_2$, were completely ineffective for the regioreversed addition.

A mechanistic rationale which accounts for the observed regioreversed addition is shown in Scheme 1; however it is highly speculative. Transmetallation from (**1**) (M = $SnBu_3$) with the aid of $AlCl_3$–Pr^iOH, presumably $AlCl_2(O\text{–}Pr^i)$, would proceed *via* an S_E2' process[4] to produce the metallated derivative (**4**), which reacts with aldehydes to give (**3**). At higher temperatures and/or over a prolonged period of time, (**4**) undergoes rearrangement to the more thermally stable isomer (**5**), which reacts with aldehydes to give (**2**). Furthermore, (**1**) itself reacts with aldehydes in the presence of $AlCl_3$ (or $AlCl_3$–Pr^iOH) to give (**2**). The reaction system would consist of the following pathways. $AlCl_3$ and other Lewis acids induce the conversion of (**1**) into (**2**) *via* path a. The relatively soft Lewis acid, $AlCl_3$–Pr^iOH, causes transmetallation to (**4**), and the reactive aldehydes react immediately to give (**3**) (path b). Relatively unreactive aldehydes and ketones permit further rearrangement to (**5**), resulting in the formation of (**2**) *via* path c.† This scheme also explains why the sequence of addition is important; the addition of aldehydes prior to the addition of (**1**) makes path a favourable. Irrespective of the precise mechanism, the present findings provide a new synthetic route to linear homoallyl alcohols.

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2 For the most recent reviews, see Y. Yamamoto and K. Maruyama, *Heterocycles*, 1982, **18**, 357; R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 555; A. Pelter, *Chem. Soc. Rev.*, 1982, **11**, 191.

3 With hindered ketones, the α-adduct is sometimes obtained because of the reversible addition of allylic organometallic reagents; R. A. Benkeser, M. P. Siklosi, and E. C. Mozdzen, *J. Am. Chem. Soc.*, 1978, **100**, 2134. (η^3-1,1-Dimethylallyl)-nickel bromide reacts with benzil to give the α-adduct, but does not react with compounds such as cyclohexanone or cyclohexenone; L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. Siiralla-Hansen, *J. Org. Chem.*, 1975, **40**, 593. We have recently successfully achieved the regioreversed addition *via* the Mg–Al system; Y. Yamamoto and K. Maruyama, *J. Org. Chem.*, 1983, **48**, 1564.

4 There do not appear to be any reports on the regiochemistry of such a transmetallation. See also, A. Hosomi, H. Iguchi, and H. Sakurai, *Chem. Lett.*, 1982, 223; A. Gambaro, P. Ganis, D. Marton, V. Peruzzo, and G. Tagliavini, *J. Organomet. Chem.*, 1982, **231**, 307.

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† We have carefully checked that the reaction occurs under kinetic control. The ratio of (**3**):(**2**) does not change if the reaction is quenched at −78 or 0 °C.