Tetrahedron Letters,Vol.27,No.21,pp 2395-2396,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

REDUCTIVE GENERATION OF ACTIVE ZERO-VALENT TIN IN $SnCl_2$-Al SYSTEM AND ITS USE FOR HIGHLY DIASTEREOSELECTIVE REACTION OF CINNAMYL CHLORIDE AND ALDEHYDES.

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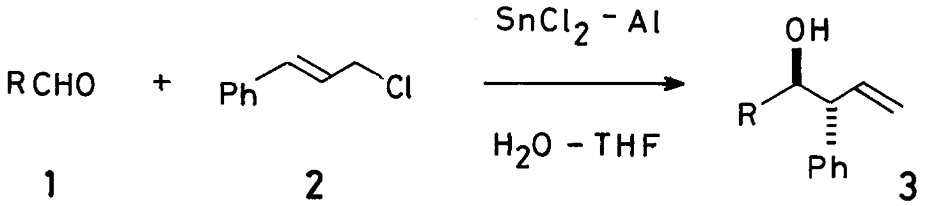
Summary; Highly diastereoselective reaction of cinnamyl chloride with aldehydes was achieved by the use of active zero-valent tin generated in $SnCl_2$-Al system.

Reactions of the well-designed allylic organometallics of silicon, chromium, boron, and etc with aldehydes provide the corresponding homoallylic alcohols with high diastereoselectivity1). Not only the high stereoselectivity and yield, but also a facile synthetic procedure are essential for any feasible synthetic methodologies. Recent Coxon's communication2) on the Sn-Al3) mediated diastereoselective reaction of cinnamyl chloride with aldehydes has prompted us to describe our simple method on $SnCl_2$-Al system which creates a higher reactivity along with complete diastereocontrol and high yield in a neutral medium.



Into a suspension of commercial grade aluminium powder (2 mmol) and tin(II) chloride (1 mmol) in THF (2.5 ml)- H_2O (1 ml) was added a mixture of aldehyde (2.4 mmol) and cinnamyl chloride (2 mmol), and the mixture was stirred at 45-50 °C for 2 h. Neither use of Lewis acids nor replacement of air in a reaction vessel with an inert gas is required. This reaction affords threo isomers exclusively for aryl and alkyl aldehydes. α , β-Unsaturated aldehydes provide 1,2-adducts with a less diastereo-preference. This stereochemistry is consistent with those of cinnamyltriphenyltin4) and crotylchromium reagent5) but opposite to cinnamyltrimethylsilane6) and crotyltributyltin7) where acyclic transition state is proposed. It is noteworthy that the present tin reagent-mediated reaction exhibits a high stereocontrol even in an aqueous solvent.

Use of tin(II) chloride is essential in the present purpose. Thus, metal tin combined with aluminium powder was employed to give 36% of **3** although the diastereoselectivity is satisfactory (96:4)[2]. The reaction rate (12h) was slower than that (2h) of $SnCl_2$-Al system so that hydrolysis of cinnamyl chloride took place as a side reaction, resulting in the formation of cinnamyl alcohol **4** (40%)[8]. The action of either tin(II) chloride or metal tin in the absence of aluminium resulted in only 8% of **3** and 83% of **4**, or 45% of **3** and 52% of **4** after 24 h stirring, respectively. These results clearly demonstrate that zero-valent tin generated by reduction of tin(II) chloride with aluminium is responsible for effective oxidative addition of cinnamyl chloride.

Table Yields and Diastereoselectivities of **3**

RUN	aldehyde	total yield (%)[a]	threo : erythro	J (Hz)[c]
1	C_6H_5CHO	82	98 : 2	7.6
2	p-Cl-C_6H_4CHO	84	99 : 1	7.8
3	p-CH_3-C_6H_4CHO	80	98 : 2	7.8
4	n-$C_6H_{13}CHO$	75	98 : 2	7.1
5	i-C_3H_7CHO [b]	68	99 : 1	7,6
6	$CH_3CH=CHCHO$ [b]	70	90 : 10	6.3
7	$C_6H_5CH=CHCHO$	80	92 : 8	6.5

a; yield of threo and erythro, b; **1** : **2** = 4 : 1 , c; $J_{CH(OH)-CH(Ph)}$ of 3(threo)

References and Notes

1) R. W. Hoffmann, Angew. Chem., Int. Ed. Engl., 21, 555 (1982); Y. Yamamoto and K. Maruyama , Heterocycles, 18, 357 (1982).

2) J. M. Coxon, S. J. van Eyk, and P. J. Steel, Tetrahedron Lett., 26, 6121 (1985). Neither yield of **3** nor diastereoselectivity is described. Yield of **3** obtained by the action of tin(0) with aluminium powder is moderate (see text).

3) J. Nokami, J. Otera, T. Sudo, and R. Okawara, Organometallics, 2, 191 (1983).

4) M. Koreeda and Y. Tanaka, Chem. Lett., 1299 (1982).

5) T. Hiyama, K. Kimura, and H. Nozaki, Tetrahedron Lett., 22, 1037 (1981).

6) T. Hayashi, K. Kabeta, I. Hamachi, and M. Kumada, Tetrahedron Lett., 24, 2865 (1983).

7) Y. Yamamoto, H. Yatagai, Y. Isihara, N. Maeda, and K. Maruyama, Tetrahedron, 40, 2239 (1984).

8) Addition of HBr in the medium resulted in 57% of **3** (97:3) and 31% of **4**, after 3 h stirring.

9) The authors are grateful to the Ministry of Education, Science, and Culture for a financial support by a Grant-in-Aid (No 60219020).

(Received in Japan 25 February 1986)