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SELECTIVE REDUCTION OF ALDEHYDES IN PRESENCE OF A KETONE WITH CHLOROTRIMETHYLSILANE AND NICKEL BORIDE

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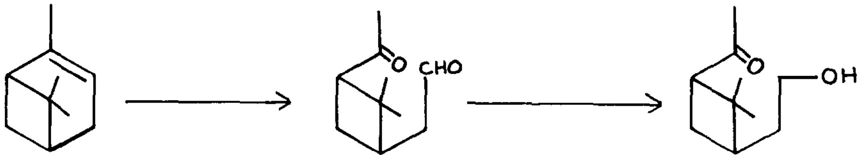
Summary - It has been shown that a combination of chlorotrimethylsilane and nickel boride effects the chemoselective reduction of an aldehyde in presence of a ketonic carbonyl group.

Hydrosilanes have been employed for the reduction of different functionalities especially in combination with a suitable catalyst but have got limited applications thus far[1]. We argued that trimethylsilane can be generated *in situ* from chlorotrimethylsilane (CTMS) and nickel boride (Ni_2B) and therefore decided to study the reductions in a medium containing hydrosilane and nickel boride as a catalyst. It was observed that CTMS-Ni_2B combination reduces aldehydes most easily and in an efficient manner (see Table 1). When the reduction of the aldehydes at entry **1**, **2**, **3**, **7** & **9** was carried out in presence of cholestanone, the latter was recovered in 92-95% yield at the end of reaction period proving the chemoselectivity of this procedure. Besides this, compound(**2**) prepared from α-pinene (**1**) was subjected to reaction conditions described in the procedure below and the product (**3**) was obtained in 95% yield further demonstrating the usefulness of our method. It may be mentioned here that nickel boride alone does not effect the reduction of aldehydes.



(**1**) (**2**) (**3**)

General procedure :

To a solution of nickel chloride (10 m mol) in 4 ml DMF/diglyme is added sodium borohydride (4 m mol) in small portions with stirring at r.t. Immediate formation of the black precipitate of nickel boride is observed with the evolution of hydrogen. After 5 min, 1.0 ml of CTMS is added and stirring continued for another 0.5 hr followed by addition of an aldehyde (1 m mol). The reaction mixture is stirred for one hr and then worked up by adding water followed by extraction with chloroform. Evaporation of the solvent furnishes the corresponding alcohol.

Numerous methods exist for chemoselective reduction of an aldehyde in presence of a ketonic carbonyl group[2] but each has its own limitations and therefore the new methodology described above will make note of.

Table 1 : Reduction of aldehydes with CTMS/Ni_2B

Entry	Aldehyde	Product[a]	Solvent	Yield[b] (%)
1	Hydroxycitronellal	Hydroxycitronellol	diglyme	90
2	Geranial	Geraniol	-do-	80
3	4-Methoxybenzaldehyde	4-Methoxybenzyl alcohol	-do-	75
4	Cinnamaldehyde	Cinnamyl alcohol	-do-	95
5	Benzaldehyde	Benzyl alcohol	-do-	95
6	3-Chlorobenzaldehyde	3-Chlorobenzyl alcohol	DMF	95
7	2-Hydroxybenzaldehyde	2-Hydroxybenzyl alcohol	-do-	95
8	$CH_3(CH_2)_{14}CHO$	$CH_3(CH_2)_{14}CH_2OH$	-do-	98
9	3-Acetoxybenzaldehyde	3-Acetoxybenzyl alcohol	-do-	90
10	3-Hydroxybenzaldehyde	No reaction	-do-	-
11	2-Nitrobenzaldehyde	No reaction	-do-	-

[a] Products were characterised by comparison (TLC, GLC, IR, NMR & Mass) with authentic samples.

[b] Yields were determined by GLC.

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References :

1. Y. Nagai, Org. Prep. Prod. Int., 12, 13 (1980).
2. C.S. Rao, A.A. Deshmukh and B.J. Patel, Ind. J. Chem., 25B, 626 (1986).

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