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A NOVEL REDUCTION SYSTEM —— $SbCl_3$-Al/ OR $SbCl_3$-Zn/DMF-H_2O FOR CONVERSION OF ALDEHYDES TO ALCOHOLS [#]

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Summary: $SbCl_3$-Al/DMF-H_2O and $SbCl_3$-Zn/DMF-H_2O were found to be an efficient reduction system for the conversion of a variety of aldehydes to alcohols.

Only a few reports have ever appeared in literatures concerning the use of organoantimony compounds in organic synthesis[1]. We have found some of their applications[2-4]. In the presence of Lewis acid, diphenylstibine reacted with carbonyl compounds to afford, after hydrolysis, alcohols in excellent yields[5]. Recently, an indirect electroreduction of acetophenone to 1-phenylethanol in the presence of $SbCl_3$ was reported by Ikeda[6]. In the course of our studies on the Barbier-type allylation of aldehydes mediated by $SbCl_3$-Fe or -Al[7], we found that $SbCl_3$-Al/DMF-H_2O (system A) and $SbCl_3$-Zn/DMF-H_2O (system B) were effective reducing systems for conversion of aldehydes to alcohols in excellent yields. When the reduction was carried out in DMF-D_2O, the aldehydes were converted to deuterium labelled alcohols (RCHDOH) conveniently.

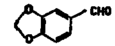
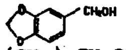
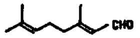
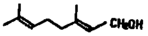
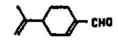
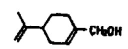
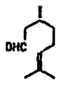
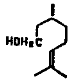
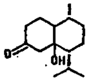
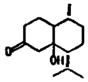
Scheme

$$\mathrm{RCHO} \xrightarrow[\mathrm{DMF\text{-}H_2O(or\ DMF\text{-}D_2O)}]{\mathrm{SbCl_3\text{-}Al\ or\ SbCl_3\text{-}Zn}} \mathrm{RCH_2OH\ (or\ RCHDOH)}$$

A mixture of $SbCl_3$ (1.2mmole), Al or Zn dust (4mmole), an aldehyde (1mmole) in a mixed solvent DMF-H_2O (1:1, 4ml) was stirred at r.t. under nitrogen. After the reaction completed (monitored by TLC), usual work up, yielded the corresponding alcohol. When the reaction was carried out in DMF-D_2O instead of DMF-H_2O, the corresponding deuterium labelled alcohol was obtained.

As can be seen in Table 1, a variety of aldehydes were reduced smoothly with both reduction systems. In system A, the reaction proceeded faster than in system B. With α,β-unsaturated aldehydes, reduction occurred only at the C=O position (No. 9 and 10), remaining the carbon-carbon double bonds intact. Neither unconjugated double bond nor cyclic ketone was attacked (No. 9~12). When a mixture of benzaldehyde and acetophenone was allowed to react with system A or B, the former was reduced preferentially.

Table 1 Reduction of aldehydes with (A) $SbCl_3$-Al/DMF-H_2O or (B) $SbCl_3$-Zn/DMF-H_2O

No,	Aldehyde	Reduction system	Reaction time(hrs)	Product*	Isolated yield(%)
1	C_6H_5CHO	A(B)	0.5(3)	$C_6H_5CH_2OH$	98(90)
2	p-ClC_6H_4CHO	A(B)	0.3(3)	p-$ClC_6H_4CH_2OH$	98(90)
3	p-$CH_3C_6H_4CHO$	A(B)	0.8(3)	p-$CH_3C_6H_4CH_2OH$	98(96)
4	p-$CH_3OC_6H_4CHO$	A(B)	2(12)	p-$CH_3OC_6H_4CH_2OH$	98(60)
5		A	1		98
6	$CH_3(CH_2)_8CHO$	A(B)	3(4)	$CH_3(CH_2)_8CH_2OH$	98(94)
7		A(B)	2(4)		95(85)
8		A	1		95
9		A(B)	1(3)		98(95)
10		A(B)	2(5)		50(80)
11		(B)	(4)		(96)
12		A	6		0

* All the products were confirmed by ^1H NMR, MS.

The reaction mechanism is not clear at present, some experimental results are noteworthy. In the absence of H_2O or antimony trichloride, the reaction did not occur. A dark precipitation, which probably involves the reduction of Sb(Ⅲ) to Sb(0) was found in the course of the reaction. Evolution of hydrogen was also observed. The hydrogen might be produced by Al or Zn with hydrogen chloride, generated from hydrolysis of $SbCl_3$. When p-chlorobenzaldehyde was treatd with Al-HCl(2N), however, 1,2-p-chlorophenyl-1,2-ethanediol was obtained as the sole product in 65% yield and no p-chlorobenzyl alcohol was observed. Therefore, hydrogen molecule does not seem to participate in the main reduction pathway.

Because of the ready access of reagents, mild reaction conditions, easy work up, and better yields as compared with other reducing reagents, this novel method provides a facile and mild approach for the reduction of aldehydes to alcohols. Further investigation is now in progress.

References and Notes:

This paper is the 81st report on the application of elemento-organic compounds of 15th and 16th groups in organic synthesis.
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