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An Efficient Reduction System - $NiCl_2.6H_2O$-Zn/DMF-H_2O for Conversion of Aldehydes to Alcohols

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Abstract : Aldehydes were efficiently converted to the corresponding alcohols at room temperature with $NiCl_2.6H_2O$-Zn/DMF-H_2O system.

Al-$NiCl_2.6H_2O$-THF system[1,2] was used for selective reduction of the double bonds of the α,ß-unsaturated carbonyl compounds and nitroarenes. We have now found that $NiCl_2.6H_2O$-Zn/DMF-H_2O is an efficient system for reduction of various aldehydes to the corresponding alcohols in one step at room temperature with excellent yields. If $NiCl_2.6H_2O$-Zn/DMF-D_2O is used instead of $NiCl_2.6H_2O$-Zn/DMF-H_2O, the aldehydes are converted to deuterium labelled alcohols (RCHDOH) conveniently as shown below.

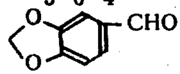
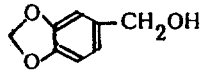
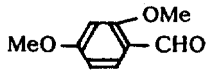
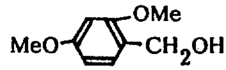
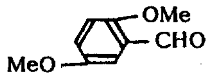
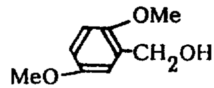
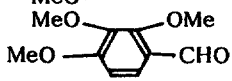
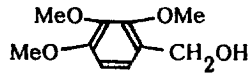
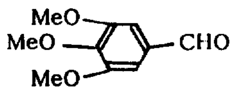
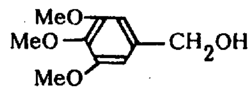
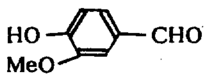
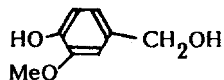
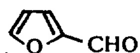
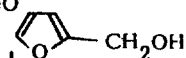
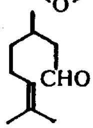
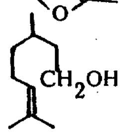
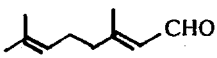
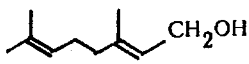
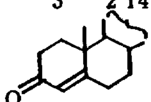
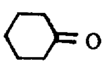
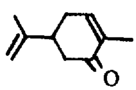
$$\mathrm{RCHO} \xrightarrow[\mathrm{DMF\text{-}H_2O\ (or\ DMF\text{-}D_2O)}]{\mathrm{NiCl_2.6H_2O}} \mathrm{RCH_2OH\ (or\ RCHDOH)} \qquad \text{Scheme}$$

The advantages of this method are - (i) the reagents are readily accessible, (ii) the reaction is carried out at room temperature in one step, (iii) yields are quite satisfactory. This method therefore also provides a facile and mild approach for reduction of aldehydes. However, ketones are found uneffected by this reagent under this condition.

The mechanism of the reaction is not clear but some experimental results are noteworthy. A dark precipitation was found in the course of the reduction which is most probably due to the reduction of Ni(II) to Ni(0).[3] In the absence of $NiCl_2.6H_2O$ or H_2O, the reduction did not occur. Evolution of hydrogen was observed which might be produced by Zn with hydrogen chloride generated from hydrolysis of $NiCl_2$.

General procedure : A mixture of $NiCl_2.6H_2O$ (3 mmol), Zn dust (10 mol), an aldehyde (1 mmol) in a mixed solvent DMF-H_2O (1:1, 4 ml) was stirred at r.t. under nitrogen. After completion of the reaction (monitored by TLC) and usual work up furnished the corresponding alcohols, which were purified by chromatography. When DMF-D_2O was used instead of DMF-H_2O, the corresponding deuterium labelled alcohols were obtained. Typical examples are compiled in the Table 1.

Table 1 : Reduction of aldehydes with $NiCl_2.6H_2O$-Zn/DMF-H_2O

Entry	Substrate	Product[a]	Time	% yield[b]
1	C_6H_5CHO	$C_6H_5CH_2OH$	30 min	95
2	p-ClC_6H_4CHO	p-$ClC_6H_4CH_2OH$	15 min	97
3	p-$CH_3C_6H_4CHO$	p-$CH_3C_6H_4CH_2OH$	30 min	95
4			1 h	98
5			1.5 h	98
6			1.5 h	98
7			2 h	98
8			2 h	98
9			2 h	95
10			2 h	95
11			5 h	95
12			2 h	95
13	$CH_3(CH_2)_{14}CHO$	$CH_3(CH_2)_{14}CH_2OH$	5 h	65
14		No reaction	3 h	
15		No reaction	1.5 h	
16		No reaction	2 h	
17	$(C_6H_5)_2CO$	No reaction	1.5 h	

[a]All products were confirmed by IR, ^1H NMR and MS
[b]Yields refer to the isolated products of > 98% purity

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