Tetrahedron Letters, Vol. 34, No. 10, pp. 1681-1684, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Cadmium Chloride-Magnesium-Water : A New System For Reduction Of Various Organic Functionalities

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Key word : Cadmium chloride-magnesium-THF-H_2O, reductions.

Abstract : Cadmium chloride-magnesium-THF-water efficiently reduced aldehydes and ketones to their corresponding alcohols, epoxide to mono-alcohol, benzyl halide to toluene, acid chloride to aldehyde and hydrolyzed thioketal to corresponding ketones.

Although a wide spectrum of reducing agents are available for the reduction of various organic functionalities[1], interest on the reductions in organic chemistry is still continuing[2]. Since the difference between the standard redox (Nernst) potentials of Cd/Cd^{++} and Mg/Mg^{++} is very high[3], we surmised that the combination of Mg-$CdCl_2$ in a protic solvent will be a useful reducing system for the reduction of organic functionalities. Our surmise was indeed found to be correct when we treated acetone with $CdCl_2$-Mg powder-water system at room temperature; instantly vigorous exothermic reaction took place which subsided after 10 minutes and isopropanol was obtained in 90% (GLC determination). Encouraged by this observation, we treated a number of ketones and aldehydes which were all reduced smoothly to the corresponding alcohol in 85-95% yield (Table-1). Interestingly, it was observed that all the α,β-unsaturated ketones and aldehydes gave corresponding allylic alcohols only.

In order to illustrate the potentiality of this system, a number of other compounds with different functionalities were exposed to $CdCl_2$-Mg-H_2O, in all cases promising results are obtained.

Reduction of epoxides by this reducing system (entry 22-24) gave the tertiary and secondary alcohols in 82% and 15% yield respectively.

Exposure of the benzyl halides (entry 25-27) to this system in THF yielded toluene quantitatively. Treatment of acid chlorides (entry 28,29) with this reducing system resulted in the formation of corresponding aldehydes (70%) with 20% of the alcohol possibly formed

Table 1 Reduction by $CdCl_2$-Mg-Water

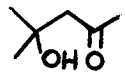
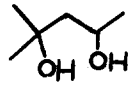
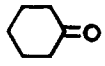
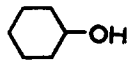
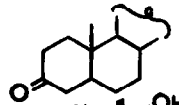
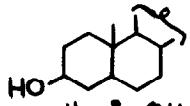
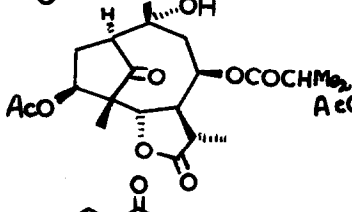
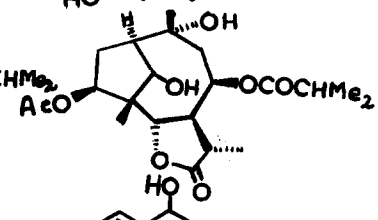
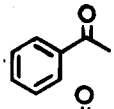
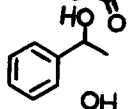
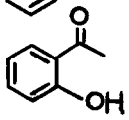
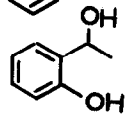
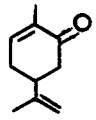
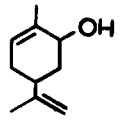
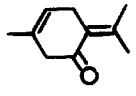
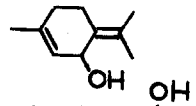
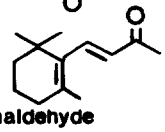
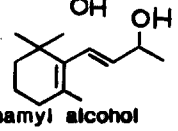
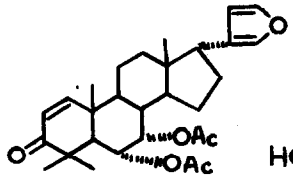
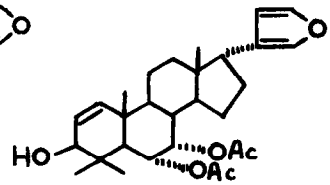
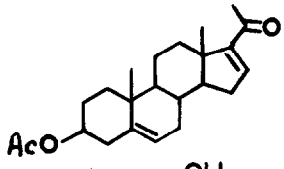
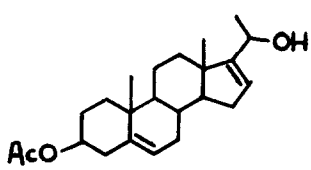
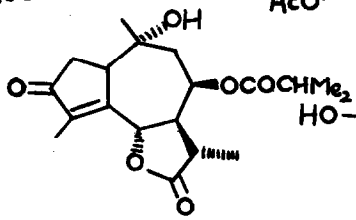
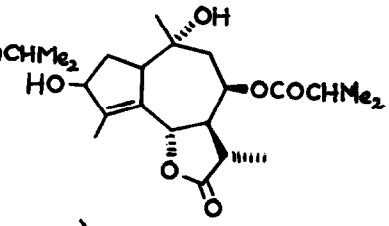
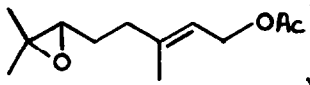
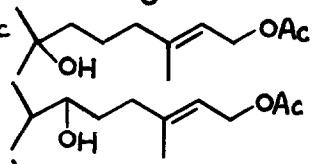
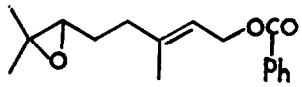
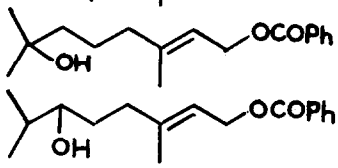
Sl No	Substrate	Product	Time(min)	Yield %[a]
1.			15	95 (GLC)
2.			15	92 (GLC)
3.			15	92
4.			15	95
5.			15	85
6.			15	95
7.			15	90
8.	n-Octadecanal	n-octadecanol	15	95
9.	Hydroxycitronellal	hydroxycitronellol	15	95
10.	Benzaldehyde	benzyl alcohol	15	96
11.	3-Hydroxy-4-methoxy-benzaldehyde	3-hydroxy-4-methoxy-benzyl alcohol	15	95
12.	Geranial	geraniol	15	95
13	But-3-en-2-one	but-3-en-2-ol	15	95 (GLC)
14.			15	95
15.			15	95
16.			15	95
17.	Cinnamaldehyde	cinnamyl alcohol	15	95
18.	Cholest-4-en-3-one	cholest-4-en-3-ol	15	94

Table 1 Reduction by $CdCl_2$-Mg-Water

Sl No	Substrate	Product	Time(min)	Yield %[a]
19.			15	94
20.			15	92
21.			15	85
22.			15	82 15
23.			15	82 15
24.	5,6-α-oxidocholestane	cholestan-5-α-ol cholestan-6-α-ol	15	82 15
25.	$PhCH_2Cl$	$PhCH_3$	15	95(GLC)
26.	$PhCH_2Br$	$PhCH_3$	15	95(GLC)
27.	$PhCH_2I$	$PhCH_3$	15	95(GLC)
28.	Oleoyl chloride	Oleic aldehyde	15	70
29.	Benzoyl chloride	benzaldehyde	15	70
30.	Cholest-4-en-3-one thioketal	Cholest-4-en-3-one	15	80
31.	But-3-en-2-one thioketal	but-3-en-2-one	15	85

a. Yield refer to the isolated yield or yield determined by GLC

from the reduction of the aldehyde produced. Most strikingly, the thioketals of cholest-4-ene-3-one (entry 30) and methyl vinyl ketone (entry 31) on exposure to this reagent system for 15 min resulted in the hydrolysis of the thioketal to give cholest-4-en-3-one and but-3-en-2-one respectively.

Although the mechanism of this reduction process is not clearly defined at this stage, the following observations were noteworthy. Anhydrous $CdCl_2$ and Mg in anhydrous THF does not react even after long exposure. But addition of few drops of water to this mixture initiates vigorous exothermic reaction with evolution of hydrogen (deuterium when D_2O is added) and the formation of metallic cadmium particles. Since $CdCl_2$ does not get hydrolyzed easily[4] and the pH of the system is about 7, hydrogen is, therefore, released from water present, possibly replaced by magnesium. When the reduction of CH_3COCH_3, $C_{17}H_{35}CHO$, $C_6H_5CH_2Cl$ and C_6H_5-COCl were carried out with this system with D_2O instead of H_2O, the deuterium incorporated product $CH_3CDODCH_3$, $C_{17}H_{35}$-CHDOD, C_6H_5-CH_2D and C_6H_5-CDO were obtained.

Thus this simple reducing system will be a useful addition to the existing methods for reduction of organic funtionalities.

Thus in a typical experiment, 1 mmol of the substrate in 3 ml of dry THF[5] was added with stirring 8 mmol of anhydrous $CdCl_2$ and 15 mmol of Mg powder. Then 100 mmol of water is added dropwise to this mixture over a period of 5 minutes. The exothermic reaction took place instantly with the liberation of hydrogen. After 15 minutes, the reaction mixture was thoroughly washed with 200 ml of CH_2Cl_2. The CH_2Cl_2 solution was dried (Na_2SO_4) evaporated under reduced pressure to give a residue which on purification by TLC gave the product characterized by spectral analysis and direct comparison with authentic compounds.

Acknowledgement : The author expresses sincere thanks to Dr R P Sharma, Dy. Director, CIMAP, Lucknow for constant encouragement and the Director, RRL Jorhat for provision of facilities.

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5. The reaction was carried out with other protic solvent such as CH_3OH, EtOH, glycols, diglymes and in each case the yield was found to be same.

(Received in UK 10 November 1992)