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(Acridine)(tetrahydroborato)zinc Complex [$Zn(BH_4)_2$(acr)]: A New Stable and Efficient Reducing Agent

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ABSTRACT

(Acridine)(tetrahydroborato)zinc complex[$Zn(BH_4)_2$(acr)] has been prepared by complexation of oneequimolar amounts of zinc tetrahydroborate and one equimolar amounts of acridine at room temperatureas gray stable reducing agents. Also, [$Zn(BH_4)_2$(acr)]has been used for reduce of different carbonyl compounds such as aldehydes, ketones, α, β-unsaturated carbonyl compounds, acyloins and a-diketones to their corresponding alcohols in excellent yields (85-95%). The reduction reactions have been carried outwithin 30-120 min by using of 0.5-1 equivalents of [$Zn(BH_4)_2$(acr)] in CH_3CN at room temperature or under reflux conditions.

Key words: $Zn(BH_4)_2$, Acridine, Reduction, Carbonyl Compounds.

INTRODUCTION

$Zn(BH_4)_2$is unique because of a) the coordination ability of Zn^{2+}, b) it'ssolubility in aprotic solventssuch as THF, Et_2O and DME, c) an efficient chemo-, regio- and stereoselective reducing agent.So,it's using and application is interesting in organic synthesis[1-2].

Several Combination reducing systems of $Zn(BH_4)_2$ such as $Zn(BH_4)_2$/TMEDA[3a], $Zn(BH_4)_2$/Me_3SiCl[3b], $Zn(BH_4)_2$/TFA/DME[3c], $Zn(BH_4)_2$/H_2O[3d], $Zn(BH_4)_2$/Al_2O_3[3e], $Zn(BH_4)_2$/C [3f], $Zn(BH_4)_2$/2NaCl[3g], $Zn(BH_4)_2$/U.S.[3h], and $Zn(BH_4)_2$/$ZrCl_4$[3i]are interesting and have been used for different reduction purposes.However, zinc tetrahydroborate has been used less than regular reducing agents in laboratory, probably because of a) non-availability as a commercial reagent b) being freshly prepared. So, $Zn(BH_4)_2$, has been modified as stable complexes such as [$Zn(BH_4)_2$(dabco)][4], [$Zn(BH_4)_2$(pyz)]$_n$[5], [$Zn(BH_4)_2(PPh_3)$] &[$Zn(BH_4)_2(PPh_3)_2$][6], [$Zn(BH_4)_2$(bpy)][7], [$Zn(BH_4)_2$(py)][8], [$Zn(BH_4)_2XP_4$][9], [$Zn(BH_4)_2$(nmi)][10a], [$Zn(BH_4)_2$(nic)][10b] and [$Zn(BH_4)_2$(caf)][10c].

In continuation of our interest for preparation of new modified tetrahydroborates, we have prepareda new stable ligand-zinc tetrahydroborate*i.e.* (acridine) (tetrahydroborato) zinc complex; [$Zn(BH_4)_2$(acr)]. Also, in this context,we have investigated the ability of [$Zn(BH_4)_2$(acr)] for the reduction of carbonyl compounds such as aldehydes, ketones,acyloins, a-diketones to their corresponding alcohols.

RESULTS AND DISCUSSIONS

We examined the reduction of benzaldehyde as a model reaction. Among the tested different solvents benzaldehyde reduction was better in CH_3CN. Our experiments showed that using 0.5 molar equivalents of $[Zn(BH_4)_2(acr)]$ in CH_3CN (3 mL) is the best conditions. Then, $[Zn(BH_4)_2(acr)]$ has been used for reduce of different aldehydes under optimized reaction conditions (Table 1, entries 1-9). All reduction reactions were completed within 30-60 min by 0.5 molar equivalents of $[Zn(BH_4)_2(acr)]$ in excellent yields of products(92-95%).

Our next attempt was the reduction of ketones. We optimized the reaction conditions with acetophenone as model compound. The reduction of ketones require a higher molar amounts of $[Zn(BH_4)_2(acr)]$ because the reactivity of ketones is lower than aldehydes. The reduction reactions were carried out with 1 molar equivalents of $[Zn(BH_4)_2(acr)]$ at reflux conditions in CH_3CN. All reductions were completed within 80-120 min with high to excellent yields of products (85-93%) as shown in Table 1 (entries 10-17).

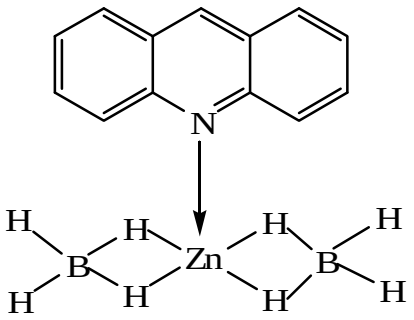
We also investigated the potential of the 1,2-reduction of α,β-unsaturated aldehydes and ketones with $[Zn(BH_4)_2(acr)]$. The reduction of cinnamaldehyde with 0.5 molar equivalents of the $[Zn(BH_4)_2(acr)]$ exclusivity afforded the 1,2-reduction product after 40 min at room temperature in CH_3CN. In this reaction, cinnamyl alcohol was obtained in 95% yield (Table 1, entry 18). Under this protocol, reduction of conjugated ketones such as benzylidenacetone (Table 1, entry 19) and chalcone (Table 1, entry 20) were achieved efficiently with 1 molar equivalents of $[Zn(BH_4)_2(acr)]$ at reflux conditions in CH_3CN in excellent yields (95-96%). The efficiency of $[Zn(BH_4)_2(acr)]$ has been compared with other reported reducing systems (Table 2). In all cases$[Zn(BH_4)_2(acr)]$ has a good potential for the reduction of organic carbonyl compounds.

EXPERIMENTAL

All substrates and reagents were purchased from commercially sources with the best quality and used without further purification. IR and ^1H NMR spectra were recorded on PerkinElmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. The products were characterized by their ^1H NMR or IR spectra and comparison with authentic samples (melting or boiling points). Organic layers were dried over anhydrous sodium sulfate. All yields referred to isolated pure products. ^1H NMR &TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Preparation of (Acridine)(tetrahydroborato)zinc Complex;$[Zn(BH_4)_2(acr)]$

An ethereal solution of $Zn(BH_4)_2$ (0.16 M, 250 mL) was prepared from $ZnCl_4$(5.452 g, 0.04 mol) and $NaBH_4$ (3.177 g, 0.084 mol)according to an available procedure in the literature[10]. Then, acridine (7.17 g, 0.04 mol) in ether (50 mL) was added dropwise to the ethereal solution of $Zn(BH_4)_2$ and stirred for 30 min. Evaporation of the solvent under vacuum at room temperature gave $[Zn(BH_4)_2(acr)]$ as a withe powder in a quantitative yield (10.08 g, 92%). Found: Zn: 23.2 %, B: 7.3 %. Calculated for $C_{13}H_{17}B_2NZn$, Zn: 23.84 %, B: 7.88%. Scheme 1.



Scheme 1: (Acridine)(tetrahydroborate) zinc complex

Reduction of Acetophenone to 1-phenylethanol with $[Zn(BH_4)_2(acr)]$, A Typical Procedure

In a round-bottomed flask (10 mL), equipped with a magnetic stirrer, a solution of acetophenone (0.120 g, 1mmol) in CH_3CN (3 mL) was prepared. The complex reducing agent (0.274 g, 1mmol) was then added as a solid and the mixture was stirred at reflux conditions. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O : 5/2).

Table 1: Reduction of a Variety of Carbonyl Compounds such as Aldehydes (entries 1-9), Ketones (entries 10-14), a-diketones (15-16), Acyloins (entriy 17) and α, β-unsaturated carbonyl Compounds (entries 18-20) to their Corresponding Alcohols with [$Zn(BH_4)_2$(acr)] as Reducing Agent in CH_3CN

Entry	Substrate	Product	Molar Ratio		
			Substrate/ [$Zn(BH_4)_2$(acr)]	Time/ min	Yield[c]/ %
1[a]	benzaldehyde	benzyl alcohol	1:0.5	30	95
2[a]	4-chlorobenzaldehyde	4-chlorobenzyl alcohol	1:0.5	30	92
3[a]	4-bromobenzaldehyde	4-bromobenzyl alcohol	1:0.5	30	95
4[a]	2,4-dichlorobenzaldehyde	2,4-dichlorobenzyl alcohol	1:0.5	30	94
5[a]	4-methylbenzaldehyde	4-methylbenzyl alcohol	1:0.5	50	95
6[a]	4-methoxybenzaldehyde	4-methoxybenzyl alcohol	1:0.5	60	92
7[a]	2-methoxybenzaldehyde	2-methoxybenzyl alcohol	1:0.5	60	94
8[a]	3-methylbenzaldehyde	3-methylbenzyl alcohol	1:0.5	60	95
9[a]	4-nitrobenzaldehyde	4-nitrobenzyl alcohol	1:0.5	30	92
10[b]	acetophenone	1-phenylethanol	1:1	90	93
11[b]	benzophenone	diphenylmethanol	1:1	120	90
12[b]	9*H*-fluoren-9-one	9*H*-fluoren-9-ol	1:1	120	91
13[b]	cyclohexanone	cyclohexanol	1:1	80	90
14[b]	4-phenylcyclohexanone	4-phenylcyclohexanol	1:1	80	85
15[b]	benzil	1,2-diphenyl ethane-1,2-diol	1:1	80	90
16[b]	1,2-bis(4-methoxyphenyl) ethane-1,2-dione	1,2-bis(4-methoxyphenyl) ethane-1,2-diol	1:1	80	90
17[b]	benzoin	1,2-diphenyl ethane-1,2-diol	1:1	90	90
18[a]	cinnamaldehyde	3-phenyl-2-propen-1-ol	1:1	40	95
19[b]	benzylideneacetone	Phenyl-3-butene-2-ol	1:1	90	90
20[b]	chalcone	4-phenyl-3-butene-2-ol	1:1	120	92

[a] The reactions have been carried out at room temperature. [b] The reactions have been carried out under reflux conditions.[c] Yields refer to isolated pure products.

Table 2: Comparison of the Reduction of Aldehydes and Ketones by $[Zn(BH_4)_2(acr)]$ in CH_3CN with other Reported Reducing Agents

Entry	Reducing Systems	Molar Ratio (Reagent./Substrate), Time/h					
		Benzaldehyde	Acetophenone	Benzophenone	Cyclohexanone	9*H*-fluoren-9-one	Benzoin
1	$[Zn(BH_4)_2(acr)]$	0.5, 0.5	1, 1.5	1, 2	1, 1.3	1 , 2	1, 1.5
2[10c]	$[Zn(BH_4)_2(caf)]$	0.5, 0.5	1, 1	1, 1.5	1, 0.5	1 , 1.5	1, 1
3[4]	$[Zn(BH_4)_2(dabco)]$	0.75, 0.7	1.2, 5.4	1.5, 8.5	-	1.5, 2.3	1, 0.17
4[5]	$[Zn(BH_4)_2(Ph_3P)]$	-	2, 1.25	-	2, 1	2, 0.5	-
5[7]	$[Zn(BH_4)_2(bpy)]$	0.25, 0.2	0.35, 0.17	1, 0.75	0.5, 0.15	1, 1.5	0.5, 0.08
6[8]	$[Zn(BH_4)_2(py)]$	1, 0.5	2, 2	2, 4.3	2, 2	2, 5.3	0.5, 0.5
7[5]	$[Zn(BH_4)_2(pyz)_n]$	1, 2.5	4, 30	-	4, 18	-	3, 5
8[10a]	$[Zn(BH_4)_2(nmi)]$	1, *Im*	1, *Im*	-	1, 1	1.6, 18	-
9[10b]	$[Zn(BH_4)_2(nic)]$	1, 0.25	2, 0.8	2, 21.5	-	-	-
109	$[Zn(BH_4)_2XP_4]$	1, 8	2, 15	2, 48	2, 24	-	-

After completion of the reaction in 90 min, a solution of 5% HCl (5 mL) was added to the reaction mixture and stirred for 10 min. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 afforded the pure liquid benzyl alcohol (0.113 g, 93% yield).

CONCLUSION

In this context, we have shown that $[Zn(BH_4)_2(acr)]$ reduces a variety of carbonyl compounds to their corresponding alcohols in high to excellent yields. Reduction reactions were carried out with 0.5-1 molar equivalents of $[Zn(BH_4)_2(acr)]$ at room temperature and reflux conditions in CH_3CN without any other additive. In addition, regioselectivity of this system was also investigated with exclusive 1,2-reduction of conjugated carbonyl compounds to their corresponding allylic alcohols in high to excellent yields. Reduction of acyloins and β-diketones by this reducing system also produced the corresponding vicinal diols**.**

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