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Reduction of α-Diketones and Acyloins with $Zn(BH_4)_2/ZrCl_4$ to their Corresponding Vicinal Diols

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ABSTRACT

α-diketones and acyloins are reduced to the corresponding vicinal diols with $Zn(BH_4)_2/ZrCl_4$system in THF at room temperature.

Key words : α-Diketones, Acyloins, $Zn(BH_4)_4$, $ZrCl_4$

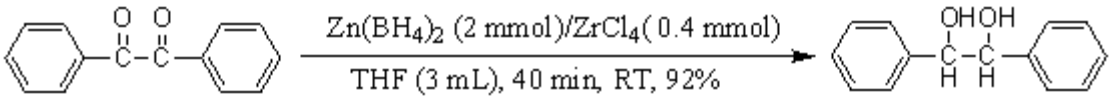
INTRODUCTION

Reduction of α-hydroxy ketones and α-diketones to vicinal diols and/or acyloins are the subject of interests in organic synthesis[1]. Reduction of α-diketones usually gives a mixture of α-hydroxy ketonesand vicinal diols. On the other hand, using of some reagents (chemical or biochemical) can undergo selective reduction of α-diketones to only α-hydroxy ketones or vicinal diols[2-6].However, Cryptococcus macerans[7], modified tetra-hydroborate agents [8a], $NaBH_4$/DOWEX1-X8[8b] system and $NaBH_4$/DOWEXRWX4[8c]have been reduced á-diketonesand acyloins to vicinal diols. In addition, reduction of acyloins to vicinal diolshas been achieved by using$H_2/CuCr_2O_4$atroom temperature[9].

RESULTS AND DISCUSSIONS

Recently, we have demonstrated that $Zn(BH_4)_2$ is a sufficient reducing agent for the reduction of carbonyl compounds under different combination systems such as $Zn(BH_4)_2/H_2O$[10], $Zn(BH_4)_2/C$[11], $Zn(BH_4)_2/Al_2O_3$[12]and $Zn(BH_4)_2$/2NaCl[13]. So, In this context and in continuing our efforts for the development of new reducing systems [10-14], we wish to introduce $Zn(BH_4)_2/ZrCl_4$ as a new combination reducing system for fast and efficient reduction of acyloins and α-diketones to their corresponding vicinal diols. The model reaction has been selected by reduction of benzil to 1,2-diphenylethane-1,2-diol. This reaction was carried out in different solvents, different molar ratio of the $Zn(BH_4)_2/ZrCl_4$for the selection of appropriate conditions at room temperature. Among the tested

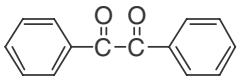
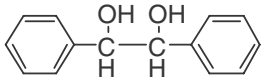
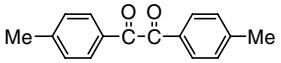
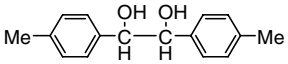
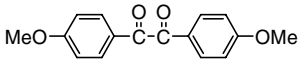
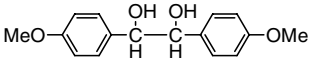
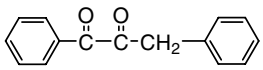
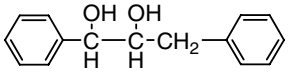
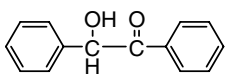
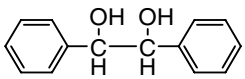
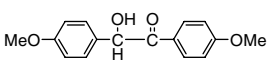
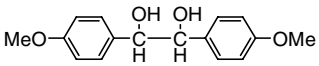
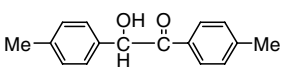
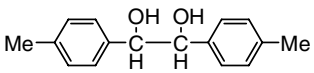
different solvents, the reaction was most facile and proceeded to give the highest yield in THF. The optimization reaction conditions showed that using 2 molar equivalents of $Zn(BH_4)_2$ and 0.4 molar equivalents of $ZrCl_4$in THFwas the best conditions to complete the reductionof benzil (1 mmol). Our observation reveals that reduction reaction completes within 40 min with 92% yields of product as shown in scheme 1.



Scheme 1:

This procedure was also applied for the reduction of various α-diketones tothe corresponding vicinal diols(Table 1, entries 1-4). All reductions were completed within 40-50 min by 2 molar equivalents of $Zn(BH_4)_2$and 0.4 molar equivalents of $ZrCl_4$in excellent yields of products(92-95%).Our next attempt was the reduction of α-hydroxy ketones to the corresponding vicinal diols. The reduction of acyloins to their corresponding vicinal diols (94-96%) was also obtained successfully by 2 molar equivalents of $Zn(BH_4)_2$ in the presence of 0.4molar equivalents of $ZrCl_4$within 50-60 minat room temperature in THF (Table 1, entries 5-7).Our attempts for reduction of α-diketones to acyloins were unsatisfactory and only vicinal diols were identified as thesole products.

Table 1:Reduction of α-diketones (1 mmol) oracyloins (1 mmol) to their corresponding vicinal diols with the Zn(BH4)2(2 mmol)/ZrCl4 (0.4 mmol) system in THF (3 mL) at room temperature

Entry	Substrate	Product	Time (min)	Yielda(%)
1			40	92
2			50	95
3			50	95
4			40	94
5			50	94
6			60	96
7			60	96

[a]Yields refer to isolated pure products.

EXPERIMENTAL

IR and ^{1}H NMR spectra were recorded on PerkinElmer FT-IR RXI and 400 MHz Bruker spectrometers, respectively. The products were characterized by their ^{1}H NMR or IR spectra and comparison with authentic samples (melting or boiling points). TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Typical Procedure for the Reduction of α-Diketones and Acyloins with $Zn(BH_4)_2/ZrCl_4$ System in THF

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer bar, a solution of benzil (0.21 g, l mmol) was prepared in THF (3 mL). To this solution, $ZrCl_4$ (0.4 mmol, 0.93 g) and $Zn(BH_4)_2$ (0.19 g, 2mmol) was added. The resulting mixture was stirred at room temperature for 40 min. The reaction was monitored by TLC (eluent:CCl_4/Et_2O:5/2). After completion of the reaction, distilled water (6 mL) was added to the reaction mixture and stirred for 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded crystals of 1,2-diphenyl ethane-1,2-diol (0.19 g, 92% yield).

CONCLUSION

In this context, we have shown that the $Zn(BH_4)_2/ZrCl_4$ as new reducing system is convenient for the reduction of α-hydroxy ketones and α-diketones to their corresponding vicinal diols. Reduction reactions were carried out with $Zn(BH_4)_2$(2mmol) and $ZrCl_4$(0.4mmol) in THF at room temperature. Short reaction times, low reaction temperature and easy work-up procedure makes as an attractive new protocol for the reduction of α-diketones and acyloinsto their corresponding vicinal diols, therefore it could be a useful addition to the present methodologies.

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