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Zinc-Promoted Reduction of 1,2-Diketones: A Simple, Efficient, and Mild Approach to α-Hydroxy Ketones

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Summary. 1,2-Diketones were readily converted to α-hydroxy ketones in high to excellent yields using zinc in saturated ammonium chloride solution.

Keywords. Zinc; 1,2-Diketones; α-Hydroxy ketones.

Introduction

α-Hydroxy Ketones are very useful synthons in organic chemistry [1]. Although the oxidation of enolates or their equivalents is a method of choice [2], the reduction of 1,2-diketones [3] also offers a useful and convenient approach. Problem arise from overreduction of diketones to diols [4] and sometimes to monoketones [5].

Conversions of 1,2-diketones to α-hydroxy ketones employing *Grignard* reagents [6], titanium(IV) chloride [7], active uranium [8], and titanium(IV) iodide [9] have been reported. The electrochemical reduction of benzil to benzoin in *DMF* has been studied as a function of *pH* [10]. Each of these methods has its merits and drawbacks.

In spite of several contributions using zinc as a reducing agent [11], for example in the *Clemmensen* reduction [12], literature lacks reports using zinc under mild and non-acidic conditions. Therefore, research in this field is still in demand.

Results and Discussion

In this communication we report that zinc in aqueous ammonium chloride can efficiently reduce 1,2-diketones to the corresponding α-hydroxy ketones. Under optimum conditions, benzoin was obtained in excellent yield when benzil was treated with zinc powder in *THF*-saturated aqueous ammonium chloride. Regarding the choice of solvent, *THF* proved to be the best. To assess the generality of

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Table 1. Reduction of 1,2-diketones to α-hydroxy ketones using zinc in *THF*-saturated aqueous ammonium chloride

$R^{a,b}$	Reaction time (min)	Yield/%^{c}
Ph	40	97
4-MePh	50	92
4-MeOPh	60	94
4-BrPh	45	90
CH_3	70	95
$-CH_2CH_2CH_2CH_2-$	45	92

[a] All substrates were purchased from commercial sources; [b] all products were characterized by comparison of their physical and spectroscopic data with those of known compounds; [c] yields refer to isolated products

the method, various 1,2-diketones were tested (Table 1). The reactions were in most cases completed within 10–60 minutes, as evidenced by the disappearance of the metal.

In conclusion, the zinc promoted reduction of 1,2-dicarbonyl compounds in aqueous media is remarkably efficient, rapid, selective, and affords high yields methodology. Compared to other methods [6–9], the present protocol is experimentally simple and inexpensive.

Experimental

Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Philips Pu 9800 FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-90A spectrometer at 90 and 22.6 MHz. All products are known compounds; their physical and spectroscopic data were compared with those of authentic samples and found to be identical.

General procedure

Zn powder (4 mmol, 0.260 g) and 2 mmol of an appropriate 1,2-diketone were slurried in 5 cm^3 saturated aqueous NH_4Cl and 5 cm^3 *THF*. The mixture was stirred at ambient temperature for the indicated time during which the Zn powder disappeared. The solutions were evaporated to dryness under reduced pressure. The crude product was extracted with diethyl ether. The solvent was evaporated; solid products were recrystallized from EtOH, liquid products were chromatographed on silica gel (AcOEt:hexane = 1:4) to afford the α-hydroxy ketones (Table 1).

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