
New Reduction Method of α -Diketones, Oxo amides, and Quinones with Zn-EtOH in the Presence of a Salt

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The reagent, Zn-Salt-EtOH effectively reduces α -diketones, oxo amides, and quinones to hydroxy ketones, hydroxy amides, and hydroquinones, respectively.

Previously we reported that Zn-ZnCl₂-EtOH (reagent I) is an effective reagent for the hydrogenation of a double bond between two carbonyl or two cyano groups, and of the double bond of indenone and cyclopentadienone.¹ We have now found

that the reagent I also effectively reduces α -diketones, oxo amides, and quinones to hydroxy ketones, hydroxy amides, and hydroquinones, respectively, and that ZnCl₂ can be replaced by various other salts.

Table 1. Yields of the reduction of (1) to (2) with reagents I and II by heating under reflux for 1 h

(1) R	Yield (%) of (2)	
	Reagent I ^a	Reagent II ^b
a Ph	89	90
b 3,4-Ethylenedioxyphenyl	84	92
c 2-Furyl	43	82
d Me	71	20

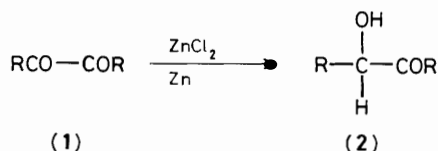
^a Reagent I: Zn–ZnCl₂–EtOH. ^b Reagent II: Zn–NaCl–MeOH–H₂O.

Table 2. Yields of the reduction of (8) to (9) with reagents I and II by heating under reflux for 1 h

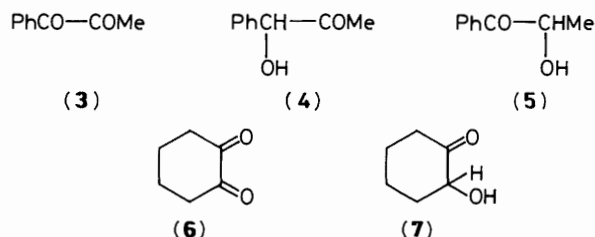
(8)	Yield (%) of (9)	
	Reagent I	Reagent II
a R ¹ = Ph, R ² = R ³ = Pr ⁱ	89	— ^a
b R ¹ = Ph, R ² R ³ = (CH ₂) ₅	60	—
c R ¹ = Ph, R ² = H, R ³ = CH ₂ Ph	12	76
d R ¹ = R ² = R ³ = Me	95	—

^a No reaction occurred.

When the diketones (1) (1 g), ZnCl₂ (1 g), and EtOH (10 ml) were heated under reflux for 1 h, the hydroxy ketones (2) were obtained in the yields shown in Table 1. This reaction proceeds under milder conditions than those reported for a similar reaction.² For example, (1a) when heated with Zn in DMF–



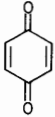
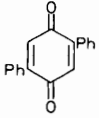
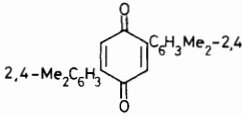
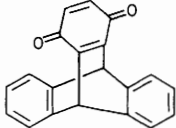
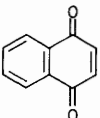
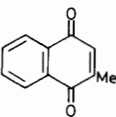
H₂O under reflux for 6 h gave (2a) in 93% yield.² Since the reaction does not proceed in the absence of ZnCl₂, Zn²⁺ might play an important role as a Lewis acid in the reduction. However, ZnCl₂ can be replaced by a wide variety of salts such as LiCl, NaCl, NaBr, NaClO₄, NaOAc, KCl, SnCl₂, CaCl₂, and NH₄Cl. For example, Zn–NaCl–50% aqueous MeOH (reagent II) is also effective in the reduction of (1) (Table 1). Since NaCl is only a weak Lewis acid, its co-ordination to (1) is not likely to be important, and its role is probably that of an electrolyte.



Some minor differences in behaviour between I and II were observed. Reduction of (3) with II gave (4) and (5) in 68 and 17% yields, respectively, although the reduction with I gave only (4) in 20% yield. Although the reduction of (6) with II gave (7) in 97% yield, the reduction with I gave a complex mixture of products.

The reduction can be done using a catalytic amount of salt, although it takes a longer time to complete. For example, when the reduction of (1a) (1 g) with Zn (1 g) was carried out under reflux in 50% aqueous MeOH in the presence of NaCl in amounts of 1, 0.1, and 0.01 g, it took 1, 1.5, and 3.5 h, respectively, to complete the reaction.

Table 3. Yields of the reduction of quinones to hydroquinones with reagent I by heating under reflux

Quinone	Reaction time (h)	Yield (%) of hydroquinone
(10) 	1	80
(11) 	4	92
(12) 	1	99
(13) 	1	70
(14) 	1.5	81
(15) 	1	53

Reduction of the oxo amides (8) to the hydroxy amides (9) can be achieved with I, except that for (8c), II is more effective (Table 2). Although the reduction of (8) to (9) can be carried out with NaBH₄, the reduction with the cheaper reagent I has an advantage in cost.



Quinones are also reduced by reagent I. Treatment of quinones (1 g) with Zn (1 g)–ZnCl₂ (1 g) in EtOH (10 ml) under reflux gave hydroquinones in the yields shown in Table 3, which compare favourably with the reagent, CrCl₂–HCl–aqueous acetone, which has also been used for quinone reduction.³ For example heating (10) and (14) under reflux with the CrCl₂ reagent under N₂ for 1 h gives the corresponding hydroquinones in 87 and 26% yields, respectively.³ The reduction with I proceeds under milder conditions, I is easier to prepare, and I is applicable to the reduction of many kinds of quinones.

References

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