

ZnO: a versatile agent for benzylic oxidations

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Abstract—Zinc oxide catalyzed oxidation of various alkylbenzenes, naphthalene and 1,2,3,4-tetrahydronaphthalene in air using microwave irradiation or conventional heating in the presence of *N,N*-dimethylformamide is described.

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1. Introduction

Oxidation is a fundamental transformation in organic synthesis.^{1–4} Benzylic oxidation holds a unique place because of its application in industry and academia. Laboratory scale liquid-phase benzylic oxidations are generally carried out with a large excess of chromium or manganese reagents.³ The metal residues are environmentally undesirable and often cause problems during work-up. Recently, nickel-catalyzed benzylic oxidation of toluenes was reported.⁵ Other reagents, which have been used include ceric ammonium nitrate in aqueous acetic acid or in HClO₄,⁶ potassium bromate,⁷ chromium trioxide in acetic anhydride,⁸ selenium dioxide,⁹ chromyl chloride,¹⁰ silver(II)oxide in phosphoric acid,¹¹ potassium permanganate adsorbed on alumina,¹² and 3,6-bis(triphenylphosphonium)cyclohexene peroxodisulfate.¹³ Many of these reagents are quite expensive and suffer from harsh reaction conditions. Thus, there is a need to develop procedures, which use inexpensive and non-toxic oxidizing agents. Recently, we have reported¹⁴ solvent-free benzylic oxidations using a urea–hydrogen peroxide complex under microwave irradiation.

The most preferred of reagents would be those which are easy to handle, inexpensive, non-toxic and easily removed during work-up. Zinc oxide is a non-toxic, inexpensive and non-hygroscopic white powder. It has been used for a number of organic syntheses in combination

with other metal oxides. For instance, zinc oxide in combination with CuO and alumina has been employed for the catalytic oxidation of phenols, *t*-BuOH and methylvinyl ketone;¹⁵ a mixture of CuO, ZnO and TiO₂ has been concerned as catalyst for the hydrogenation of cyclic aliphatic esters and alcohols;¹⁶ ZnO in combination with CuO has been involved in the preparation of *N*-cyclohexylaniline from aniline and cyclohexanol;¹⁷ ZnO in combination with Cu and Cr₂O₃ has served for methanol synthesis;¹⁸ Fe–ZnO catalyst was used for the oxidative dehydrogenation of *n*-butane to butene;¹⁹ a mixture of ZnO, CuCl₂, CaCO₃ and MgCO₃ was advocated as an additive for preventing clinker formation during coal combustion;²⁰ copper zinc oxide catalyst has been used for ambient temperature carbon monoxide oxidation;²¹ ZnO in combination with CaCO₃ and SiO₂ has been employed for preparing UV-resistant plastic master batch.²²

The coupling of microwave (MW) irradiation²³ with the use of catalysts or mineral-supported reagents provides chemical processes with special attributes such as enhanced reaction rates, higher yields, better selectivity and improved ease of manipulation.

Since ZnO is easily available and non-toxic, we wish to report here some efficient ZnO mediated benzylic oxidations under air under MW irradiation using small amounts of DMF, or by conventional heating in an oil-bath equipped with a thermostat using DMF as solvent. To the best of our knowledge, ZnO has not yet been reported as catalyst/mediator for benzylic oxidations. This method provides a noticeable improvement over other existing method as ZnO is not toxic or expensive, work-up being simply reduced to filtration followed

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by treatment with crushed ice. Furthermore, ZnO has been shown to interact efficiently with MW radiation to reach 326 °C within 5.5 min when submitted to MW exposition in a commercial oven at a 1 kW emitted power.²⁴

The experimental conditions for the oxidation of toluene to benzoic acid were explored either in the absence of solvent or in the presence of DMF or *o*-dichlorobenzene (DCB) under MW irradiation, since these solvents interact strongly with microwaves due to their high polarities. The oxidation efficiency of ZnO was determined on the basis of the amount of ZnO and solvent used. The results are summarized in Table 1.

In the absence of solvent, no reaction was observed within 6 min while good results were obtained in the presence of DMF. The work-up procedure is indeed easy, requiring only treatment with crushed ice. In addition, there is no alteration in the yield from 0.25 to 1 equiv of DMF except a slight decrease in the irradiation period.

ZnO intervention for benzylic oxidations proved necessary, since no reaction occurred when the oxidation of toluene was performed using either DMF or DCB in the absence of ZnO under MW irradiation (Table 1, entries 8 and 9) for up to 8 min. Furthermore, the necessity of oxygen (air) was evaluated by carrying out the oxidation of toluene (10 mmol) under nitrogen in the presence of ZnO (2.5 mmol) and DMF (5 mL for oil-bath and 2.5 mmol for MW heating) by stirring in an oil-bath at 90 °C or irradiating in a MW oven. No reaction was observed by TLC even after 5 h in the case of oil-bath or 6 min in the case of MW heating, whereas an 83% yield was obtained when 10 mmol of toluene was irradiated under MW together with DMF (2.5 mmol) and ZnO (2.5 mmol) in open vessels.

Table 1. Conditions and results for the ZnO-mediated oxidation of toluene to benzoic acid under MW irradiation

Entry	Experimental conditions ^a			Isolated yield ^c (%)	Temperature (°C) ^d
	Solvent	mmol	Time (min) ^b		
1	—	—	6	No reaction	72
2	DMF	2.5	6	83	95
3	DMF	5.0	4.5	82	100
4	DMF	10.0	4.25	84	107
5	DCB	2.5	5	45	100
6	DCB	5.0	7	47	105
7	DCB	10.0	6.25	46	107
8 ^e	DMF	2.5	8	No reaction	90
9 ^e	DCB	2.5	8	No reaction	98
10 ^f	DMF	2.5	6	No reaction	96

^a The experiments were carried out by mixing toluene (10 mmol) and ZnO (2.5 mmol) with the solvent.

^b Reaction time for which maximum yields were achieved.

^c Mean value of three experimental runs.

^d Temperature evaluated at the end of exposure during MW experiment by immersing a glass thermometer into the reaction mixture and was an approximate temperature range.

^e Experiment conducted without the presence of ZnO.

^f Experiment conducted under nitrogen atmosphere.

Subsequently, this method was extended to various substituted toluenes bearing electron-withdrawing or electron-donating groups, providing the corresponding benzoic acids in fairly good to excellent yields (Table 2).

After establishing that benzylic oxidations were performed successfully under MW irradiation, efforts were made to conduct these reactions using conventional heating in which DMF was chosen as solvent and the reaction temperature kept at 90 °C. The best conditions were obtained when toluene (10 mmol), ZnO (2.5 mmol) and DMF (5 mL) were stirred in a pre-heated oil-bath at 90 °C, affording benzoic acid in 81% yield. This method was extended to substituted toluenes, yielding the corresponding benzoic acids in moderate to excellent yields. Significant results for ZnO-mediated benzylic oxidations under both MW irradiation or oil-bath heating are summarized in Table 2. In general, yields obtained with MW irradiation were significantly improved (10–18% points) (entries 3, 5, 9–15) when compared to oil-bath experiments conducted at 90 °C.

We then studied the use of ZnO for the selective oxidations of one of the methyl groups in dimethylbenzene simply by regulating the amount of ZnO and heating conditions. As a typical example, in the case of 1,2-dimethylbenzene (Table 2, entry 5), when 2.5 mmol of ZnO was used, 2-methylbenzoic acid was obtained in 80% yield under MW exposure within 8 min and 65% yield using oil-bath heating within 1.5 h. However, if the amount of ZnO was doubled, 1,2-dimethylbenzene (Table 2, entry 6) gave phthalic acid in 89% yield using microwaves for 5 min and 75% yield using oil-bath heating for 2 h. Similarly, in the case of 1,4-dimethylbenzene (Table 2, entries 7 and 8), 4-methylbenzoic acid and terephthalic acid can be obtained selectively using either MW irradiation or oil-bath heating.

In the case of toluenes containing an acetoxy group at the 2-, 3- or 4-position (entries 11–13), the reaction proceeded selectively to give 2-, 3- or 4-acetoxybenzoic acids and no phenol (hydrolysis product) was detected by TLC. Furthermore, toluenes substituted at the 3- or 4-position by electron-withdrawing groups such as a nitro moiety were oxidized smoothly to the corresponding benzoic acids in excellent yield (entries 3 and 4). Toluene substituted by electron rich groups (entries 5–8 and 11) also underwent the oxidation efficiently. In the case of ethylbenzene, where there is a possibility of formation of acetophenone,¹⁷ the reaction took place exclusively to provide benzoic acid and no acetophenone was detected by TLC. The present mild method was also successful for the oxidation of naphthalene and tetralin to phthalic acid, for which generally highly drastic conditions are required.

In order to check the possibility of specific non-thermal MW effect for the ZnO-mediated oxidation of alkylbenzenes, we carried out the oxidation of toluene (Table 2, entry 1) using a pre-heated oil-bath at 95 °C (temperature measured at the end of the reaction in the MW oven) for 6 min keeping all other conditions identical to the MW experiment. It was found that no reaction

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