

Retraction Notice

Title of retracted article: Water-Soluble Copper Complex Catalyzed Solvent-Free Green Oxidation of Alkylarenes with *tert*-Butyl Hydroperoxide

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History

Expression of Concern:

 yes, date: yyyy-mm-dd no

Correction:

 yes, date: yyyy-mm-dd no**Comment:**

The paper is withdrawn from "Modern Research in Catalysis" due to personal reasons from the corresponding author of this paper.

This article has been retracted to straighten the academic record. In making this decision the Editorial Board follows COPE's [Retraction Guidelines](#). The aim is to promote the circulation of scientific research by offering an ideal research publication platform with due consideration of internationally accepted standards on publication ethics. The Editorial Board would like to extend its sincere apologies for any inconvenience this retraction may have caused.

Editor guiding this retraction: Anita LIU (Editorial Assistant of MRC)

Water-Soluble Copper Complex Catalyzed Solvent-Free Green Oxidation of Alkylarenes with *tert*-Butyl Hydroperoxide

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ABSTRACT

Different benzylic compounds were efficiently oxidized to the corresponding ketones with aqueous 70% *tert*-butyl hydroperoxide (TBHP) and the catalytic system composed of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC). The catalytic system $\text{CuCl}_2/\text{BQC}/\text{TBHP}$ allows obtaining high yields at room temperature under solvent-free conditions. The interest of this system lies in its cost effectiveness and its benign nature towards the environment. Benzylic *tert*-butylperoxy ethers and benzylic alcohols were observed and suggested as the reaction intermediates. Analysis of organic products by atomic absorption did not show any contamination with copper metal. In terms of efficiency, CuCl_2/BQC system is comparable or superior to the most of the catalytic systems described in the literature and which are based on toxic organic solvent.

Keywords: Oxidation; Water-Soluble Catalyst; Copper Chloride; *tert*-Butyl Hydroperoxide; Alkylarenes; 2,2'-Biquinoline-4,4'-Dicarboxylic Acid Dipotassium Salt

1. Introduction

Ketones are one of the most important classes of organic compounds. They are used as solvents and precursors to a variety of polymers and biologically active compounds such as pharmaceuticals, flavors, agrochemicals, and fragrances. Furthermore, the occurrence of ketone moiety is widespread among natural products. Ketones are frequently prepared by different methods including, Friedel-Crafts acylation of aromatics, ozonolysis, hydration of alkynes, Weinreb-Nahn synthesis [1], Kornblum-DeLamare rearrangement [2], cross-coupling between dialkylcuprate and acyl chlorides, Reaction of organolithium and Grignard with nitriles, oxidation of alcohols including Oppenauer-type reaction [3], and oxidation of methylenes.

The oxidation of hydroxyl and methylene groups to the corresponding carbonyl moieties remains one of the most fundamental and indispensable reactions in organic synthesis [4,5]. For such processes, the utilization of at least stoichiometric amounts of often toxic oxidants, es-

pecially chromium (VI) reagents, remains widespread [6]. Safety hazards associated with these oxidants and their toxic by-products, and the difficulty to work-up the reaction mixtures are the major problems of such processes. As a consequence for the increasing demand for cleaner, efficient, and environmentally friendly oxidations, different catalytic methods using small amounts of metallic derivatives and clean oxidants have been developed [4,7,8]. Thanks to its price relatively low and its reduced form which can be recycled, *tert*-butyl hydroperoxide (TBHP) has been studied for benzylic oxidation in combination with different transition-metal catalysts such as Cr, Co, Mn, Fe, Ru, Rh, Au, and Cu [7-27]. Despite the economic and environmental benefits of copper-based catalysts compare to the other transition metals that are either toxic or very expensive, their use for benzylic oxidations is not abundant [28,29]. With all these metals, the vast majority of catalytic processes are, unfortunately, performed in costly and toxic organic solvents. Furthermore, in the homogeneous processes, the separation of the catalysts from the reaction products and their quantitative recovery in an active form are cumbersome. Very

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few organic solvent-free processes have been reported for benzylic oxidation with TBHP [26,27]. However, these processes are based on high temperatures and are limited to very few substrates. Aqueous organometallic catalysis that was emerged as an active field of research in green chemistry is an excellent approach to overcome these drawbacks [30-33]. The use of water as solvent is important for economical, safety, and environmental reasons. The water-soluble catalyst which operates and resides in water is easily separated from the reaction products by simple decantation. In addition, the products are not contaminated with traces of metal catalyst, and the use of organic solvents, such as benzene and chlorinated hydrocarbons is circumvented. Despite the evident ecological and economical advantages of aqueous phase catalysis, to the best of our knowledge there are no reports concerning selective oxidation of alkylarenes to benzylic ketones in water at room temperature and based on copper catalysts. In the past years, we developed different catalytic transformations in water including the hydration of nitriles to the corresponding amides catalyzed by $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{P}(\text{m-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (TPPTS) [34], the transfer hydrogenation of aldehydes and ketones with isopropanol catalyzed by water-soluble rhodium complexes [35], Oppenauer-type oxidation of alcohols [36,37], and reductive amination of ketones [38]. We disclosed also the water-soluble CuCl_2/BQC as a highly effective catalyst for the oxidation of secondary benzylic, allylic, propargylic, and 1-heteroaryl alcohols with TBHP [39,40], and for the oxidation of alkynes to the corresponding ynones [41]. The catalytic system is very cheap, stable and can be recycled several times without significant loss of activity. The above mentioned advantages of CuCl_2/BQC coupled with those of TBHP prompted us to investigate the catalytic activity of $\text{CuCl}_2/\text{BQC}/\text{TBHP}$ system for the oxidation of benzylic methylenes to the corresponding carbonyl moieties. In this paper we are pleased to report our results regarding this unprecedented, general, and highly efficient organic solvent-free catalytic oxidation of alkylarenes.

2. Experimental

2.1. Materials and Instruments

All the substrates, Copper chloride dihydrate, 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC), tetrabutylammonium chloride (TBAC), sodium carbonate, and aqueous 70% *tert*-butyl hydroperoxide were purchased from Aldrich Chemical Co. and used without further purification.

Routine NMR measurements were performed on a Bruker AC-200 spectrometer at 200 MHz and 50 MHz, respectively, for ^1H and ^{13}C , using TMS as internal stan-

dard and CDCl_3 as solvent.

2.2. Typical Procedure for the Oxidation of Alkylarenes

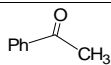
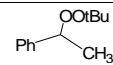
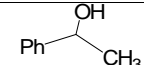
Into an open 25 mL round-bottom flask charged with distilled water (5 mL), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.02 mmol), Na_2CO_3 (0.14 mmol), and BQC (0.02 mmol), was added TBAC (0.06 mmol). The green-blue solution was stirred for 5 minutes then the substrate (2 mmol) was introduced followed by aqueous 70% TBHP (4 to 8 mmol). The purple mixture was allowed to react for 17 hours at room temperature. At the end of the reaction, the mixture is still purple. The products and substrate, which are not soluble in water, were extracted three times with ethyl acetate (20 mL). The combined organic layers were dried (MgSO_4), evaporated to dryness, and then analyzed by thin layer chromatography, ^1H NMR and ^{13}C NMR. Conversions and yields were determined after the reaction mixtures were purified using column chromatography (silica gel) with a gradient of petroleum ether/ethyl acetate (100 to 95/5) as the eluant.

3 Results and Discussion

In our preliminary experiments we investigated the oxidation of ethylbenzene (1). Thus, the oxidation of 1 (2 mmol) with aqueous 70% *tert*-butyl hydroperoxide (2 equivalents, 4 mmol) in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.02 mmol), BQC (0.02 mmol), tetrabutylammonium chloride (0.06 mmol), and Na_2CO_3 (0.14 mmol) in distilled water, proceeds smoothly at room temperature, will full conversion, affording acetophenone (79%), 1-*tert*-butylperoxy-ethylbenzene (11%), and 1-phenylethanol with 10% yield (Table 1, entry 1). The catalytic activity and yields were not affected by scaling up the oxidation to a gram-scale of substrate (Table 1, entry 2). When the reaction was performed using 3 and 4 equivalents of TBHP, the amounts of acetophenone collected increased in detriment of 1-*tert*-butylperoxy-ethylbenzene and 1-phenylethanol which decreased markedly, and 98% yield was achieved with 4 equivalents of TBHP (Table 1, entries 3 and 4). Since we demonstrated in our previous works that the catalytic system can be recycled efficiently for the oxidation of alcohols [39] and propargylic methylenes [41], no recycling experiments have been attempted in this project. The analysis of organic products by atomic absorption, however, did not show any contamination of acetophenone with copper.

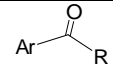
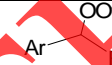
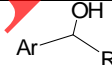
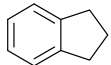
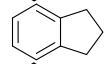
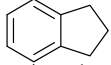
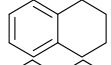
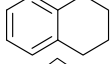
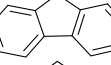
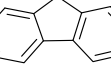
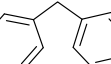
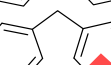


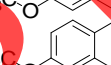
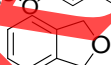
To evaluate the synthetic potential of CuCl_2/BQC system, various alkylarenes were subjected to the oxidation with two to four equivalents of aqueous 70% TBHP. Thus, indane (2), tetralin (3), fluorene (4), diphenylmethane (5), deoxybenzoin (6), 6-methoxytetralin (7), and phthalan (8) were studied, and the best results are summarized in Table 2. The oxidation of benzylic me

Table 1. Oxidation of ethylbenzene (1) with aqueous 70% TBHP catalyzed by CuCl₂·2H₂O/BQC^a.

Entry	TBHP (equiv)	Conversion (%)	Yield (%)		
					
1	2	100	79	11	10
2 ^b	2	100	76	12	10
3	3	100	84	8	6
4	4	100	98	Traces	Traces

^aReaction conditions: Ethylbenzene (2 mmol), BQC (0.02 mmol), CuCl₂·2H₂O (0.02 mmol), Na₂CO₃ (0.14 mmol), TBAC (0.06 mmol), aqueous 70% TBHP (4 to 8 mmol), water (5 mL), RT, 17 hours. ^bThe reaction was up scaled 5 times.

Table 2. Oxidation of various alkylarenes with aqueous 70% TBHP catalyzed by CuCl₂·2H₂O/BQC^a.

Entry	Substrate	TBHP (equiv)	Conversion (%)	Yield (%)		
						
1		2	100	92	3	2
2		3	100	98	Traces	Traces
3 ^b		3	94	64	15	12
4		2	80	56	12	10
5		4	94	77 ^c	10	Traces
6		2	89	84	5	0
7		3	100	100	0	0
8		3	85	79	5	0
9		4	93	86	7	0
10		4	94	94	0	0
11		2	78	56 (39/17) ^d	14 ^e	8 ^f
12		4	98	58 (50/8) ^{d,g}	20 ^e	0
13 ^h		2	100	70	-	-

^aReaction conditions: Substrate (2 mmol), BQC (0.02 mmol), CuCl₂·2H₂O (0.02 mmol), Na₂CO₃ (0.14 mmol), TBAC (0.06 mmol), aqueous 70% TBHP (4 to 8 mmol), water (5 mL), RT, 17 hours. ^bThe reaction was performed without Na₂CO₃. ^c2,3-Dihydro-1,4-naphthoquinone was also obtained in 6% yield. ^dRatio of 6-Methoxy-1-tetralone/7-methoxy-1-tetralone. ^eA mixture of 1-*tert*-butylperoxy-6-methoxytetralin and 1-*tert*-butylperoxy-7-methoxytetralin was obtained. ^fA mixture of 6-methoxy-1,2,3,4-tetrahydro-naphthalen-1-ol and 7-methoxy-1,2,3,4-tetrahydro-naphthalen-1-ol was obtained. ^g6-Methoxy-2,3-dihydro-1,4-naphthoquinone was also obtained in 12% yield. ^hOther products (intermediates) were observed in ¹H NMR spectrum.

thylenes proceeded smoothly to carbonyl moieties with excellent yields in most cases. As illustrated in **Tables 1** and **2**, ketones were obtained along with small amounts of either benzylic *tert*-butylperoxy ethers, benzylic alcohols, or both, except in the case of deoxybenzoin (**Table 2**, entry 10). Such compounds have been proven as reac-

tion intermediates for benzylic oxidations of alkylarenes with TBHP [7,8,11,16,25,28,42-43]. When the oxidation of indane was performed without catalytic amount of Na₂CO₃ acetophenone was obtained with only 64% yield (**Table 2**, entry 3). As we have previously demonstrated the absence of Na₂CO₃ is prejudicial to oxidation process

since it allows keeping CuCl₂/BQC system in its water-soluble active form [39]. Tetralin afforded, with 4 equivalents of TBHP, α -tetralone in 77% yield, *tert*-butylperoxy ether (10%), and 6% of 2,3-dihydro-1,4-naphthoquinone. The latter, as an over-oxidation product, was not formed with stoichiometric amount (2 equivalents) of TBHP (**Table 2**, entries 4 and 5). This dione was also observed in the case of Rh₂(cap)₄/anhydrous TBHP system [16]. 1,4-naphthoquinone that was formed with different chromium catalysts [8], was not detected with our system. 6-methoxytetralin behaves almost in same manner as tetralin. Using 2 equivalents of TBHP, mono ketones 6-methoxy-1-tetralone and 7-methoxy-1-tetralone were isolated respectively in 39 and 17% yields, along with the corresponding peroxides and alcohols, and no over-oxidation products were detected (**Table 2**, entry 11). Mixture of mono ketones with different ratios have been reported with CrO₃/TBHP [11-12] and Rh₂(cap)₄/anhydrous TBHP [16] systems. By increasing the amount of TBHP to 4 equivalents, yields of mono ketones did not

increase significantly. However, mono ketones ratio changed to 50/8 and 6-methoxy-2,3-dihydro-1,4-naphthoquinone was isolated in 12% yield (**Table 2**, entry 12). The oxidation of phthalan with 2 equivalents of TBHP afforded phthalide in 70% yield, with full conversion (**Table 2**, entry 13). The other products according to the analysis of the crude reaction mixture by H¹ NMR, are probably reaction intermediates mainly *tert*-butylperoxy ether. A similar intermediate was obtained in the case of the oxidations of isochroman with Rh₂(cap)₄/anhydrous TBHP [16]. No increase in the yields of phthalide was observed with longer reaction time, more TBHP, or by increasing reaction temperature.

The synthetic utility of our system is illustrated in **Table 3** where our data are compared with those of other homogeneous or heterogeneous catalytic systems described in the literature. The comparison is limited to the oxidation based on the use of an excess of TBHP (at least two equivalents to substrate), and only yields of mono ketones are indicated. In terms of efficiency, our system

Table 3. Oxidation of alkylarenes with TBHP: Comparative data from various catalytic systems.

Entry	Catalytic method ^a	Ref.	Yield of ketone (%)							
			1	2	3	4	5	6	7	8
1 ^b	CuCl ₂ ·2H ₂ O (1%)/BQC/TBHP ^c , RT, water		98	98	77	100	86	94	39/17	70
2	Cr-PILC (2.5%)/anh. TBHP ^d (2)/RT/CH ₂ Cl ₂	9	92	83	91	88	90	0		
3	(Ph ₃ SiO) ₂ CrO ₂ (5%)/TBHP (4)/RT/CH ₂ Cl ₂	10		86	88	98	79			
4	CrO ₃ (5%)/TBHP (4)/RT/BTF	11	83	92	77	99	93		57/12	
5	CrO ₃ (5%)/TBHP (7)/RT/CH ₂ Cl ₂	12		60	43	94	53		36/17	
6	Cr _E -ZSM-5 (0.2%)/TBHP (4)/80°C/PhCH ₃	13	85	93	85	87	89			
7	CrSBA-15/TBHP (2)/80°C - 120°C/PhCl	14,15		76 ^e	95 ^e	41 ^e	58 ^f			
8	Rh ₂ (cap) ₄ (1%)/anh. TBHP (5)/RT/DCE	16	20 ^g	84	60	99	55		30/30	
9	RuCl ₂ (PPh ₃) ₄ (1%)/anh. TBHP (4)/RT/PhH	17	53	51		87	71			
10	Bi (20%)/TBHP (6)/100°C/pyridine, AcOH	18		65	77	91	95			
11	FeCl ₃ (2%)/TBHP (3)/82°C/pyridine	19	17	61	41	>99				45
12	Fe(BTC)/TBHP/70°C/CH ₃ CN	20		51	44 ^h	72				
13	KAuCl ₄ (5%)/TBHP (2)/90°C/pyridine	21			58	>99	99			65
14	ANMnO ₂ (10%)/TBHP (3)/80°C/CH ₃ CN	22		89	74	100	92			
15	Co-SiO ₂ (1.25%)/anh. TBHP (6)/90°C/isooctane	23	65				58			
16	CoEPS3 (6.8%)/anh. TBHP (6)/50°C/CH ₃ CN	24				97 ^g	91			
17	Cu(AMP)Cl ₂ (1%)/TBHP (5)/50°C/CH ₃ CN	25			63					
18	LaCrO ₃ (10%)/TBHP (2)/90°C/no solvent	26		85	84	91	95			
19	Mn(TMCP)P/TBHP (3)/150°C/no solvent	27	91							

^aCatalyst (% to substrate)/TBHP (number of molar equivalents to substrate). If the amounts are not indicated between brackets, the data is not indicated in the reference paper. ^bThis work. See Table 2 for reaction conditions. ^cTBHP = aqueous *tert*-butyl hydroperoxide. ^danh. TBHP = anhydrous *tert*-butyl hydroperoxide. ^ePublished in reference 14. ^fPublished in reference 15. ^gThe reaction was performed at 40°C. ^hThe reaction was performed at 75°C.

is comparable or superior to the most of the catalytic systems described. For example, oxidation of deoxybenzoin with our system led to benzil with 94% yield, while Cr-PILC [9] system is completely inactive (Table 3, entries 1 and 2). All these catalytic systems require the use of one or more of the following conditions: toxic organic solvent, high temperature, anhydrous TBHP, or catalyst that may be toxic, expensive or difficult to synthesize. With regard to economic and environmental issues, it is largely beneficial to use our system based on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and BQC which are available commercially, cheap cost, and relatively benign. Our system is even more interesting since the ligand BQC (2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt) is cheaper than the corresponding parent ligand 2,2'-biquinoline. From Aldrich Chemical Co., BQC and 2,2'-biquinoline cost 8485 and 12,994 Canadian dollars per mole, respectively.

4. Conclusion

In conclusion, the catalytic system composed of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC), was found to be highly efficient for the selective oxidation of alkyarenes to the corresponding benzylic ketones, with aqueous 70% *tert*-butyl hydroperoxide at room temperature, under organic solvent-free conditions. This very simple catalytic system is cheap and environmentally friendly.

5. Acknowledgements

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