Research Article

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

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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 CuCl₂·2H₂O and 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC). The catalytic system CuCl₂/BQC/TBHP allows obtaining high yields at room temperature under organic 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, CuCl₂/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 dialkylicuprate 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 [4-6]. For such processes, the utilization of at least stoichiometric amounts of often toxic oxidants, especially chromium (VI) reagents, remains widespread [7]. 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 [4,8-9]. 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 [8-28]. 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 [29-30]. 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 few organic solvent-free processes have been reported for benzylic oxidation with TBHP [27-28]. 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 [31-34]. 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) [35], the transfer hydrogenation of aldehydes and ketones with isopropanol catalyzed by water-soluble rhodium complexes [36], Oppenauer-type oxidation of alcohols [37-38], and reductive amination of aldehydes [39]. 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 70% TBHP [40-41], and for the oxidation of alkynes to the corresponding yrones [42]. 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 70% TBHP prompted us to investigate the catalytic activity of CuCl\(_2\)/BQC/TBHP system for the oxidation of benzylic methylenes to the corresponding carbonyl moieties. It is important to note that aqueous TBHP (70% in water) is much safer to use compared to the explosive anhydrous TBHP that has serious safety problems regarding handling, storage and shipping [43]. In this paper we are pleased to report our results regarding this unprecedented, general, and highly efficient organic solvent-free catalytic oxidation of alkylarenes (Scheme 1).

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 \(^1\text{H}\) and \(^13\text{C}\), using TMS as internal standard 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), CuCl\(_2\), \(\text{H}_2\text{O}\) (0.02 mmol), Na\(_2\)CO\(_3\) (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, \(^1\text{H}\) NMR and \(^13\text{C}\) 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.

Ethical approval: The conducted research is not related to either human or animal use.
3 Results and Discussion

We first investigated the oxidation of indane (1) chosen as a model reaction, under different conditions. No reaction was observed in the absence of aqueous 70% t-butyl hydroperoxide (TBHP) or CuCl₂. When indane (2 mmol) was oxidized with TBHP (2 equivalents, 4 mmol) in the presence of CuCl₂ (0.02 mmol), BQC (0.02 mmol) and Na₂CO₃ (0.14 mmol) in distilled water, 1-indanone was obtained with 61% yield and 74% conversion. The other product obtained is 1-tert-butylperoxy-indane (13%) (Table 1, entry 1). When the oxidation of indane was repeated in the presence of tetrabutylammonium chloride (TBAC, 0.06 mmol) as the phase transfer catalyst, full conversion of indane was observed and 1-indanone was obtained with 92% yield along with 1-tert-butylperoxy-indane (3%) and 1-indanol (2%) (Table 1, entry 2). The positive influence of TBAC on the reaction conversion and 1-indanone yield is expected since phase transfer catalysts, such as surfactants, co-solvents and tenside ligands, have been successfully used in order to increase the reaction rates in aqueous-phase organometallic catalysis [40,42,44]. Also, in our previously reported oxidation of alcohols [40] and alkynes [42] with TBHP/CuCl₂/BQC, we demonstrated that the addition of water-soluble co-solvents such as methanol or acetonitrile, phase-transfer catalysts such as cyclodextrins or ammonium salts, increase reaction rates, and the best results were obtained with tetrabutylammonium chloride. A decrease in the oxidation conversion (100% to 66%) and in 1-indanone yield (92% to 30%) was observed when the reaction was performed without BQC (Table 1, entries 2-3). Sasson and al. demonstrated the formation of Cu(OH)Cl from CuCl₂ under their biphasic conditions for benzylic oxidations with TBHP/CuCl₂ system [29]. We believe that under our conditions, (BQC)Cu(OH)Cl may be formed and leads to more active water-soluble catalytic species. Sodium carbonate plays a crucial role in this catalytic process as it keeps the ligand BQC in its basic form that makes it water-soluble [40]. In distilled water, without Na₂CO₃ CuCl₂ generates an acidic solution where BQC is transformed by protonation to water insoluble 2,2’-biquinoline-4,4’-dicarboxylic acid (BQCH) that results in green water insoluble copper complex (Cu/BQCH). Under these conditions, probably there is not sufficient contact between the catalyst and the substrate, which leads to the lower yields obtained (Table 1, entries 4-5). The oxidation performed with 3 equivalents of TBHP led to an excellent yield of 1-indanone with no traces of over oxidation products such as 1,3-indandione (Table 1, entry 6).

We also investigated the oxidation of ethylbenzene (2). Thus, the oxidation of 2 (2 mmol) with 70% TBHP (2 equivalents) in the presence of CuCl₂·2H₂O (0.02 mmol), BQC (0.02 mmol), tetrabutylammonium chloride (0.06 mmol), and Na₂CO₃ (0.14 mmol), proceeds smoothly at room temperature, will full conversion, affording acetophenone (79%), 1-tert-butylperoxy-ethylbenzene (11%), and 1-phenylethanol with 10% yield (Table 2, entry 1). The catalytic activity and yields were not affected by scaling up the oxidation to a gram-scale of substrate (Table 2, 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 2, entries 3-4). Traces of benzoic acid as an over oxidation product were not detected. Since we demonstrated in our previous works that the catalytic system can be recycled efficiently for the oxidation of alcohols [40] and propargylic methylenes [42], 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 CuCl₂/BQC system, other alkylarenes were subjected to the oxidation with two to four equivalents of aqueous 70% TBHP. Thus, tetralin (3), fluorene (4), diphenylmethane (5), deoxybenzoin (6), 6-methoxytetralin (7), and phthalan

| Entry | TBHP (equiv.) | Conversion (%) | Yield (%) |
|-------|--------------|---------------|-----------|
| 1     | 2            | 74            | 61, 13    | Traces    |
| 2     | 2            | 100           | 92, 3     | 2         |
| 3     | 2            | 66            | 30, 30    | 6         |
| 4     | 2            | 75            | 50, 21    | 4         |
| 5     | 3            | 94            | 64, 15    | 12        |
| 6     | 3            | 100           | 98        | Traces    |

* Reaction conditions: indane (2 mmol), BQC (0.02 mmol), CuCl₂·H₂O (0.02 mmol), Na₂CO₃ (0.14 mmol), TBAC (0.06 mmol), aqueous 70% TBHP (4 to 6 mmol), water (5 mL), RT, 17 hours.
* The reaction was performed without TBAC.
* The reaction was performed without BQC.
* The reaction was performed without Na₂CO₃.
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 3, entry 11). The oxidation of phthahalene with 2 equivalents of TBHP afforded phthalaldehyde in 70% yield, with full conversion (Table 3, entry 12). The other products according to the analysis of the crude reaction mixture by H NMR, are probably reaction intermediates mainly tert-butylperoxy ether. A similar intermediate was obtained in the case of the oxidation of isochroman with Rh/(cap)/anhydrous TBHP [17]. No increase in the yields of phthalaldehyde was observed with longer reaction time, more TBHP, or by increasing reaction temperature.

The synthetic utility of our system is illustrated in Table 4 where our data are compared with those of other homogeneous or heterogeneous catalytic systems described in the literature. The comparison is limited to the oxidations 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 is comparable or superior to the most of the catalytic systems described. For example, oxidation of deoxybenzoin (6) with our system led to benzil with 94% yield, while Cr-PILC [10] system is completely inactive (Table 4, entries 1-2). All these catalytic systems require the use of one or more of the following conditions: toxic organic solvent, high temperature, dangerous 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 CuCl2,2H2O 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 $8,485 and $12,994 Canadian dollars per mole, respectively.

As we mentioned benzylic tert-butylperoxy ethers and benzylic alcohols have been proven as reaction intermediates for benzylic oxidations of alkylarenes with TBHP [8-9,12,17,26,29,45-46]. 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 3, entries 3-4). This dione was also observed when tetralin was oxidized with anhydrous TBHP and catalyzed by Rh/(cap), [17]. 1,4-naphtoquinone that was formed with different chromium catalysts [9], was not detected with our system. While 3 equivalents of TBHP are sufficient to lead to 100% fluorenone from fluorene, 4 equivalents of the oxidant are needed to reach excellent yields in the cases of benzophenone and benzil, respectively from diphenylmethane and deoxybenzoin (Table 3, entries 5-9). 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 3, entry 10). Mixture of mono ketones with different ratios have been reported with CrO/TBHP [12-13] and Rh/(cap)/ anhydrous TBHP [17] 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 3, entry 11). The oxidation of phthahalene with 2 equivalents of TBHP afforded phthalaldehyde in 70% yield, with full conversion (Table 3, entry 12). The other products according to the analysis of the crude reaction mixture by H NMR, are probably reaction intermediates mainly tert-butylperoxy ether. A similar intermediate was obtained in the case of the oxidation of isochroman with Rh/(cap)/anhydrous TBHP [17]. No increase in the yields of phthalaldehyde was observed with longer reaction time, more TBHP, or by increasing reaction temperature.

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As we mentioned benzylic tert-butylperoxy ethers and benzylic alcohols have been proven as reaction intermediates for benzylic oxidations of alkylarenes with TBHP [8-9,12,17,26,29,45-46]. The oxidation mechanism that we propose in Scheme 2 accounts for the formation of these intermediates, and is inspired by previously reported benzylic oxidations with TBHP and catalyzed by Cu(II) [26,29]. Initially CuCl reacts with the hydrophilic ligand BQC to form the water-soluble compound (BQC) CuCl2 (equation 1). (BQC)CuCl2 reacts with 2 equivalents of TBHP to generate (BQC)Cu(OH)Cl and tert-butylperoxy radicals (equations 2 and 3). This later complex leads to (BQC)CuCl2(OOt-Bu) after a reaction


Table 3: Oxidation of various alkylarenes with aqueous 70% TBHP catalyzed by CuCl$_2$.H$_2$O/BQC.

| Entry | Substrate | TBHP (equiv.) | Conversion (%) | Yield (%) |
|-------|-----------|---------------|----------------|-----------|
| 1     | ![Substrate 1](image1) | 4 | 100 | 98 | Traces |
| 2     | ![Substrate 2](image2) | 3 | 100 | 98 | Traces |
| 3     | ![Substrate 3](image3) | 2 | 80 | 56 | 12 |
| 4     | ![Substrate 4](image4) | 4 | 94 | 77$^a$ | 10 | Traces |
| 5     | ![Substrate 5](image5) | 2 | 89 | 84 | 5 | 0 |
| 6     | ![Substrate 6](image6) | 3 | 100 | 100 | 0 | 0 |
| 7     | ![Substrate 7](image7) | 3 | 85 | 79 | 5 | 0 |
| 8     | ![Substrate 8](image8) | 4 | 93 | 86 | 7 | 0 |
| 9     | ![Substrate 9](image9) | 4 | 94 | 94 | 0 | 0 |
| 10    | ![Substrate 10](image10) | 2 | 78 | 56 (39/17)$^c$ | 14$^d$ | 8$^a$ |
| 11    | ![Substrate 11](image11) | 4 | 98 | 58 (50/8)$^e$ | 20$^d$ | 0 |
| 12$^g$ | ![Substrate 12](image12) | 2 | 100 | 70 | - | - |

$^a$ Reaction conditions: Substrate (2 mmol), BQC (0.02 mmol), CuCl$_2$.H$_2$O (0.02 mmol), Na$_2$CO$_3$ (0.14 mmol), TBAC (0.06 mmol), aqueous 70% TBHP (4 to 8 mmol), water (5 mL), RT, 17 hours.

$^b$ 2,3-Dihydro-1,4-naphthoquinone was also obtained in 6% yield.

$^c$ Ratio of 6-Methoxy-1-tetralone / 7-methoxy-1-tetralone.

$^d$ A mixture of 1-tert-butylperoxy-6-methoxytetralin and 1-tert-butylperoxy-7-methoxytetralin was obtained.

$^e$ A 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.

$^f$ 6-Methoxy-2,3-dihydro-1,4-naphthoquinone was also obtained in 12% yield.

$^g$ Other products (intermediates) were observed in H$^1$NMR spectrum.

with TBHP (equation 4). Benzylic radical is then generated by the abstraction of the benzylic hydrogen of the substrate by t-butyloxy radical [8,9,26,29,47,48] or t-butylperoxy radical [8,21,47,48,49,50] (equations 5 and 6). Equations 7 and 8 explain the formation of tert-butylperoxy ethers and benzylic alcohols from the benzylic radical and respectively (BQC)Cu(Cl)(OOt-Bu) [26,29] and (BQC)Cu(OH)Cl [8,18,28,51]. The formation of benzylic alcohols may also be explained by the reaction of the benzylic radical with the coordinated TBHP to the copper complex (Scheme 3). This mechanism is prompted by the mechanism proposed by Muzart for chromium(VI)-catalyzed benzylic oxidation [8,9]. tert-Butylperoxy ethers (Ar)(R)CH(OOt-Bu) undergo
homolytic cleavage of C-H bond, leading to \((\text{Ar})(\text{R})\) \((\text{OOt-Bu})\text{C}\) radicals that lead to aromatic ketones through a mechanism similar to that proposed for chromium-catalyzed homolytic scission of organic peroxides to ketones with TBHP \[45\].

Previously we demonstrated that the rate-limiting step for the oxidation of alcohols to ketones with BQC/CuCl\(_2\)/TBHP system involves heterolytic C-H bond cleavage \[40\], in agreement with Sasson and al. who, in addition, suggest Cu(IV)=O as catalytic active species \[29\]. High-valent species have been reported when catalytic precursors react with TBHP \[8,18,48,52,53\] (equation 9). We thus, propose the oxidation of \((\text{BQC})\text{Cu(OH)Cl}\) with TBHP to \((\text{BQC})(\text{Cl})(\text{OH})\text{Cu}=\text{O}\) (equation 10). Then we rationalize the formation of benzylic ketones with the mechanism in Scheme 4 that involves heterolytic dehydrogenation of benzylic alcohols via six-membered cyclic transition state proposed by Muzart for chromium complexes \[8,9\].

| Entry | Catalytic method\(^a\) | Ref | Yield of ketone (%) |
|-------|------------------------|-----|---------------------|
| 1\(^b\) | CuCl\(_2\)\(2\)\(\text{H}_2\)\(\text{O}\) (1%)/BQC/TBHP\(^e\), RT, water | 1 | 98 98 77 100 86 94 39/17 70 |
| 2 | Cr-PILC (2.5%)/anh. TBHP\(^d\) (2)/RT/\(\text{CH}_2\)Cl\(_2\) | 2 | 83 92 91 88 90 0 |
| 3 | (\(\text{Ph}_2\)SiO)\(\text{CrO}_2\) (5%)/TBHP\(^d\) (4)/RT/\(\text{CH}_2\)Cl\(_2\) | 3 | 11 86 88 98 79 |
| 4 | CrO\(_3\) (5%)/ TBHP\(^d\) (4)/RT/BTF | 12 | 14 93 85 85 87 89 |
| 5 | CrO\(_3\) (5%)/ TBHP\(^d\) (7)/RT/\(\text{CH}_2\)Cl\(_2\) | 13 | 13 60 43 94 53 36/17 |
| 6 | Cr\(_2\)ZSM-5 (0.2%)/ TBHP\(^d\) (4)/80\(^o\)C/\(\text{PhCH}_3\) | 6 | |
| 7 | CrSBA-15/TBHP (2)/80-120\(^o\)C/\(\text{PhCl}\) | 15,16 | 76\(^e\) 95\(^e\) 41\(^e\) 58\(^e\) |
| 8 | Rh\(_2\)(\text{cap})\(1\)%/anh. TBHP (5)/RT/\(\text{DCE}\) | 17 | 17 84 20\(^d\) 60 99 55 30/30 |
| 9 | RuCl\(_2\)(\(\text{PPH}_3\))\(_2\) (1%)/anh. TBHP (5)/RT/PhH | 5 | 18 51 53 87 71 |
| 10 | Bi (20%)/ TBHP\(^e\) (6)/100\(^o\)C/pyridine, AcOH | 9 | 19 65 77 91 85 |
| 11 | FeCl\(_2\) (2%)/ TBHP\(^e\) (3)/82\(^o\)C/pyridine | 10 | 20 61 17 41 \(>99\) |
| 12 | Fe(BTC)/ TBHP\(^e\) /70\(^o\)C/\(\text{CH}_2\)\(\text{CN}\) | 11 | 21 51 44\(^g\) 72 |
| 13 | KAuCl\(_4\).\(0.5\)\(\text{H}_2\)\(\text{O}\) (5%)/anh. TBHP (2)/90\(^o\)C/pyridine | 12 | 22 58 \(>99\) 99 65 |
| 14 | ANMnO\(_2\) (10%)/ TBHP\(^e\) (3)/80\(^o\)C/\(\text{CH}_2\)\(\text{CN}\) | 13 | 23 89 74 100 92 |
| 15 | Co-SiO\(_2\) (1.25%)/anh. TBHP (6)/90\(^o\)C/\(\text{isooctane}\) | 14 | 24 65 58 |
| 16 | CoEPS\(_3\) (6.8%)/anh. TBHP (6)/50\(^o\)C/\(\text{CH}_2\)\(\text{CN}\) | 15 | 25 97\(^i\) 91 |
| 17 | Cu(AMP)Cl\(_2\) (1%)/ TBHP\(^e\) (5)/50\(^o\)C/\(\text{CH}_2\)\(\text{CN}\) | 16 | 26 63 |
| 18 | LaCrO\(_3\) (10%)/ TBHP\(^e\) (2)/90\(^o\)C/no solvent | 17 | 27 85 84 91 95 |
| 19 | Mn(TMCPP)/ TBHP\(^e\) (3)/150\(^o\)C/no solvent | 18 | 28 91 |

\(^a\) Catalyst (% 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.

\(^b\) This work. See Table 3 for reaction conditions.

\(^c\) TBHP = aqueous tert-butyl hydroperoxide (70%).

\(^d\) anh. TBHP = anhydrous tert-butyl hydroperoxide.

\(^e\) Published in reference 15.

\(^f\) Published in reference 16.

\(^g\) The reaction was performed at 40\(^o\)C.

\(^h\) TBHP = aqueous tert-butyl hydroperoxide (80%).

\(^i\) The reaction was performed at 75\(^o\)C.

\(^j\) TBHP = aqueous tert-butyl hydroperoxide (65%).
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\[
\begin{align*}
\text{CuCl}_2 & \xrightarrow{\text{BQC}} (\text{BQC})\text{CuCl}_2 \\
(\text{BQC})\text{CuCl}_2 + \text{t-BuOOH} & \rightarrow (\text{BQC})\text{CuCl} + \text{t-BuOO}^- + \text{HCl} \\
(\text{BQC})\text{CuCl} + \text{t-BuOOH} & \rightarrow (\text{BQC})\text{Cu(OH)}\text{Cl} + \text{t-BuO}^- \\
(\text{BQC})\text{Cu(OH)}\text{Cl} + \text{t-BuOOH} & \rightarrow (\text{BQC})\text{Cu(Cl)(OOt-Bu)} + \text{H}_2\text{O} \\
\text{t-BuO}^- + \text{R-H} & \rightarrow \text{t-BuOH} + \text{R}^- \\
\text{t-BuOO}^- + \text{R-H} & \rightarrow \text{t-BuOOH} + \text{R}^- \\
(\text{BQC})\text{Cu(Cl)(OOt-Bu)} + \text{R}^- & \rightarrow (\text{BQC})\text{CuCl} + \text{R-OOt-Bu} \\
(\text{BQC})\text{Cu(OH)}\text{Cl} + \text{R}^- & \rightarrow (\text{BQC})\text{CuCl} + \text{R-OH}
\end{align*}
\]

\textbf{Equation 1-8}

\textbf{Scheme 2}: Plausible mechanisms for the formation of \textit{t}-Butylperoxy ethers and benzylic alcohols.

\textbf{Scheme 3}: Formation of benzylic alcohols via coordinated TBHP.
In conclusion, the catalytic system composed of CuCl$_2$.2H$_2$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.

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