



Aqueous-phase catalytic oxidation, transfer hydrogenation, reductive amination and hydration reactions



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ABSTRACT

As part of our work devoted to the synthesis of organic compounds using “green” processes, we developed several water-soluble catalysts that allow efficiently the synthesis of ketones, amines, alcohols and amides. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ combined to 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC) was reported as an active catalyst for the selective oxidation with TBHP of alcohols, alkylarenes and alkynes. We developed also successfully hydrogen transfer reactions. While $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{BQC}$ proved to be efficient for Oppenauer-type oxidation of secondary alcohols, $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{P}(\text{m-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (TPPTS) showed very good activities for Meerwein–Ponndorf–Verley-type reduction of ketones and aldehydes. Higher alkylated amines and amides were also synthesized respectively, by direct reductive amination of aldehydes with primary and secondary amines catalyzed by water soluble $\text{Pd}(\text{PhCN})_2\text{Cl}_2/\text{BQC}$, and hydration of nitriles with $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$. Many of these catalytic systems are recycled with no significant loss of activity and the final products are isolated in easy manners.

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1. Introduction

Nowadays many indispensable and fundamental reactions in organic synthesis, such as oxidations and reductions, are still performed using stoichiometric amounts of harmful inorganic reagents [1]. Safety hazards associated with these reagents and their by-products, and the difficulty to work-up the reaction mixtures are the major problems that make such widespread processes not environmentally friendly and not accepted in the concept of *green chemistry*. Consequently, there is tremendous demand for new processes that satisfy increasing environmental concerns and constraints. Thus, numerous catalytic methods using small amounts of metallic derivatives have been developed [2]. Unfortunately, most of these catalytic transformations are accomplished 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 still the most important and difficult problems. Aqueous organometallic catalysis that has emerged as an active field of research in *green chemistry* is an excellent approach to overcome these drawbacks [3,4]. 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. This review summarizes recent work from our group regarding the synthesis of various organic compounds based on the concept of aqueous-phase catalysis.

2. Results and discussion

2.1. Oxidation reactions with *tert*-butyl hydroperoxide

The oxidation of carbinol and methylene groups to the corresponding carbonyl moieties remains one of the most important reactions in organic synthesis [2]. Different transition-metal catalysts such as Cr, Co, Mn, Fe, Ru, Rh, Au, and Cu has been studied for such processes, particularly benzylic oxidations with *tert*-butyl hydroperoxide (TBHP) [2,5–8]. The interest in TBHP resides in its relative stability during the oxidation reactions, its low price and its reduced form which can be recycled. 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 oxidations is not abundant [9,10]. With all these metals, the vast majority of catalytic processes are, unfortunately, performed in costly and toxic organic solvents. Very few organic solvent-free processes have been reported for benzylic oxidation with TBHP [7,8].

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However, these processes are based on high temperatures and are limited to very few substrates.

We reported that 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) is a highly effective catalyst for the oxidation of secondary benzylic, allylic, propargylic and 1-heteroaryl alcohols with TBHP in the presence of catalytic amount of tetrabutylammonium chloride (TBAC) [11,12]. The synthetic utility and limits of this catalytic system were illustrated by various alcohols. Secondary benzylic alcohols afforded selectively the corresponding ketones with full conversions. Allylic and propargylic alcohols underwent chemoselective oxidations leading to the corresponding unsaturated ketones with high yields, and no other products from epoxidation or rearrangement [13] reactions were detected. The catalytic system proved also to be able to catalyze the oxidation of unactivated alcohols, albeit in low yields (20–39%). Also, under the same conditions, the substitution of TBHP with greener oxidants, namely hydrogen peroxide (30% in water), sodium percarbonate or sodium perborate, gave no reaction. To get more insight into the catalytic activity of this oxidation method, the reaction was extended to 1-heteroaromatic-1-alkanols.

1-Heteroaromatic ketones are among the most important functionalized heterocycles that are essential precursors to a variety of biologically active compounds such as alkaloids. 1-Heteroaromatic ketones are frequently prepared by Friedel–Crafts acylation of heteroaromatic rings [14–17], condensation of metalated heterocycles with nitriles [18], and stoichiometric oxidations of 1-heteroaromatic-1-alkanols [19]. Although a plethora of catalytic methods have been developed for the oxidation of alcohols, the catalytic oxidations of 1-heteroaromatic-1-alkanols to the corresponding ketones are limited [20–22]. Our catalytic system was found to be highly efficient for the selective oxidation of secondary 1-heteroaromatic-1-alkanols to the corresponding heteroaromatic ketones, with aqueous *t*-butyl hydroperoxide at room temperature or 40 °C (Scheme 1). It is compatible with various heterocycles groups such as 1, 2 or 4-pyridyls, 2-thienyl, 2-furyl, 2-pyrrolyl and indolyl. In the case of 2-pyridylcarbinols, where the nitrogen atom is very close to the hydroxyl groups, the reactions are sluggish and very poor results were obtained at room temperature and 40 °C. Remarkably, the oxidation performed using higher catalyst/substrate ratio, and longer reaction time led to full conversion of the alcohols. The broad synthetic scope of this catalytic system was demonstrated in the synthesis of 2-ketopyrroles [14,15] and 2-ketoindoles [15–17,23] known for their biological properties, and for the synthesis of bis heteroaromatic ketones containing 2-thienyl moieties coupled with 2-pyridyl, 2-imidazolyl, or 2-thiazolyl group. These results indicate also the significant synthetic utility of our system since the oxidations of 2-pyrrolyl alcohols were performed with free (NH)-pyrroles, and there was no need to introduce protecting groups.

We further extended $\text{CuCl}_2/\text{BQC}/\text{TBHP}$ to the oxidation of benzylic [24] and propargylic [25] methylene moieties. Alkylarenes were efficiently oxidized to the corresponding benzylic ketones in high yields (58–100%) at room temperature under solvent-free conditions. Benzylic *tert*-butylperoxy ethers (0–20%) and benzylic alcohols (0–12%) were observed and suggested as the reaction intermediates. In terms of efficiency, CuCl_2/BQC system is comparable or superior to various catalytic systems described in the literature and which 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.

α,β -Acetylenic ketones are essential precursors to a variety of biologically active compounds, such as C-nucleosides [26], anti-cancer agents [27] and pheromones [28]. These conjugated ynones are highly versatile building blocks for various organic compounds

such as heterocycles [29]. α,β -Acetylenic ketones are frequently prepared by different methods including, acylation of alkynyl organometallic reagents [30], cross-coupling between terminal alkynes and acyl chlorides [31], carbonylation of terminal alkynes in the presence of aryl halides [32] and multistep synthesis [33]. α,β -Acetylenic ketones are also prepared by oxidation reactions of either propargylic alcohols or the corresponding alkynes. While the oxidation of propargylic alcohols using stoichiometric [34] or catalytic [35] processes is not frequent, direct oxidation technologies of alkynes to α,β -acetylenic ketones are scarce [36–42]. Stoichiometric and large excess amounts of chromium(VI) reagents have been used for α -oxidation of alkynes. However, low yields were obtained [36]. The first Cr(VI)-catalyzed α -oxidation of alkynes with *tert*-butyl hydroperoxide was reported, and only moderate yields were reached although large excess of TBHP used and long reaction time. In addition, the oxidation reactions were mostly performed in benzene [37]. SeO_2/TBHP system was also used for the oxidation of propargylic methylenes [38]. The internal alkynes studied underwent α,α' -oxidation which led to a mixture of mono- and di-oxygenated acetylenic alcohols and ketones, with ynones as minor products [38]. A recent report showed that alkynes were converted by aerobic oxidation into α,β -acetylenic ketones with good yields using *N*-hydroxyphthalimide combined with a transition metal [39]. Aerobic oxidations of alkynes were also performed using hydroperoxides and metallic catalysts [40,41]. Nonheme iron complexes combined to hydrogen peroxide or TBHP led to poor yields and selectivities for α,β -acetylenic ketones [40], while better results were obtained with $\text{Cu(II)}/\text{TBHP}$ system [41]. Finally iron phthalocyanines grafted onto silica were successfully used as catalysts for the oxidation of alkynes to ynones with excess TBHP [42]. To the best of our knowledge there were no reports previous to our work concerning selective α -oxidation of alkynes to α,β -acetylenic ketones in water. We, thus, disclosed an unprecedented highly efficient oxidation of alkynes to the corresponding ynones in water with aqueous *tert*-butyl hydroperoxide catalyzed by the system composed of CuCl_2 and BQC [25]. To evaluate the synthetic potential of CuCl_2/BQC system, various aromatic and aliphatic alkynes were subjected to the oxidation with four equivalents of TBHP under mild conditions (Scheme 2). Full conversions of alkynes were reached with excellent selectivities and propargylic *tert*-butylperoxy ethers were observed and suggested as the reaction intermediates. In the case of terminal alkynes the oxidations are sluggish and low yields ranging from 32 to 40% were obtained.

2.2. Hydrogen transfer oxidation and reduction

Oppenauer-type oxidation of secondary alcohols and Meerwein–Ponndorf–Verley-type (MPV-type) reduction of ketones and aldehydes are elegant and highly selective processes that can be carried out under mild conditions, and are compatible with many functional groups such as carbon–carbon double and triple bonds, halogens, amino groups or sulfur atom-containing groups. Various transition-metal complexes have been studied as catalysts for Oppenauer-type oxidations [43,44] and MPV-type reductions [45]. Despite the obvious economical and ecological importance of aqueous-phase catalysis, few catalytic systems were reported for the hydrogen transfer reduction of aldehydes and ketones using as reducing agents sodium formate [46–48] and isopropanol. In this latter case, water-soluble aminosulfonamide complexes were reported as catalysts [49]. However, the transformation was limited to acetophenones, 1-indanone and 2-acetonaphthone, and no attempts have been made to recycle the catalysts.

As part of our research program devoted to the synthesis of organic compounds in water, we were interested in developing an effective recyclable water-soluble catalyst for Meerwein–Ponndorf–Verley-type reduction. We reported that

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