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A novel, green 1-glycyl-3-methyl imidazolium chloride–copper(II) complex catalyzed C–H oxidation of alkyl benzene and cyclohexane

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Abstract

A variety of alkyl-arenes and cyclohexane were converted to the corresponding ketones with NaClO as the oxidant in the presence of 1-glycyl-3-methyl imidazolium chloride–copper(II) complex. This method contains simplified product isolation and catalyst recycling, affording benzylic C–H oxidation of alkyl-arenes imparting high yield of ketones. Furthermore, complex could be reused seven times without a significant loss of its catalytic activity.

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The oxidation of hydrocarbons is an important task due to their wide applications in both laboratory and industry. The significance of carbonyl compounds can serve as valuable building block for the manufacture of speciality chemicals in pharmaceuticals, agrochemicals and various natural products containing aryl ketones [1]. Moreover existing processes for the oxidation of hydrocarbons use toxic and often stoichiometric or excess oxidants eventually producing wastes such as, Cr (VI) [2] or KMnO₄ [3]. In the last few years, other methods have been devised for introducing a carbonyl moiety at the alkyl/aryl position, for example, copper(II) complex/H₂O₂ [4], Ir-catalyzed C–H activation/borylation [5], PhI (OAc)₂ in [bmim]PF₆/CH₂Cl₂ [6], poly(4-vinylpyridine) supported MTO [7] and HBr–H₂O₂ [8]. Though all these methods provide good yield, but some have drawbacks such as lengthy work-up procedure, harsh reaction conditions (organic co-solvents) and require absolutely dry and inert media. Thus, there is a need to develop an operationally simple, safe and widely usable eco-friendly method.

Notably, more attentions have been given to the reusable ionic compounds as solvents and catalysts in the development of cost-effective protocols. There is considerable interest in the use of room temperature ionic liquids as promising substitutes due to their tuneable polarity hydrophobicity, thermal stability and low vapour pressure. These properties of ILs lead to better solvating ability of various organic, inorganic and polymeric compounds, leading to better solvents and catalysts for many reactions [9].

As a result of their green credential and potential to enhance reaction rates and selectivities, ionic liquids are finding increasing applications in organic synthesis [10]. Recently, copper complex has been used for several organic transformations such as the epoxidation of styrene [11], oxidation of alcohol [12], alkane [13], asymmetric synthesis

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$$R \xrightarrow{[Gmim]Cl-Cu (II)}_{NaClO} \qquad R \xrightarrow{Q} R' \qquad R and R' = alkyl, aryl rt/10-12 h$$

Scheme 1. The oxidation of alkanes catalyzed by [Gmim]Cl-Cu(II) complex in NaClO.

[14], amination [15] and also for the Suzuki cross-coupling [16] reaction. From above the open literature the development of benign, non-toxic and eco-friendly catalytic alkane oxidation, based on copper functionalized ionic liquid, with NaClO is a major challenge. In this article we described a novel 1-glycyl-3-methyl imidazolium chloride–copper(II) complex/NaClO (Scheme 1) as an effective catalyst for alkylarenes and cyclohexane oxidation. Herein, we report an unprecedented, mild and simple synthetic protocol for the oxidation of alkylarenes and cyclohexane to their corresponding carbonyl compounds at ambient temperature using [Gmim]Cl–Cu(II) complex as shown in Scheme 1.

1. Results and discussion

The [Gmim]Cl–Cu(II) complex catalyzed C–H oxidation reaction was carried out at 25 °C, using ethyl benzene for model reaction to investigate different parameters, such as diverse oxidants and catalysts. Initially, the effect of different oxidants to the model reaction was studied; these results are summarized in Table 1. Obviously, there is no appreciable reaction in absence of catalyst (Table 1, entry 1). Futhermore, reaction carried with different oxidants such as *t*-BuOOH, NaClO₂, H₂O₂, and O₂ that demonstrated poor conversions; while NaClO gave good results (Table 1, entries 2–6). After conceiving the best oxidant, we further optimized the reaction conditions in presence of [Gmim]Cl–Cu(II). The experiment illustrated that on decreasing the time from 48 to 10 h gave the same results with full conversion and 85% yield of acetophenone (Table 1, entries 7–10). However, the yields were dropped appreciably on decreasing the time from 10 to 1 h (Table 1, entries 11–13). The influence of the amount of NaClO and [Gmim]Cl–Cu(II) were then investigated. When the amount of NaClO decreased from 10 to 2 mmol, the C–H could still be oxidized with a satisfactory result. However, the oxidization of ethyl benzene could not be completed with 1 mmol NaClO (Table 1, entries 14–17). It is noted that increasing the amount of ionic liquid led to increased yields of acetophenone. By all these experimental results and discussions it was concluded that 2 mmol NaClO is sufficient to brought out the complete C–H oxidation reaction in 10 h at 25 °C.

Entry	Oxidant	Time (h)	Yield ^b (%)	
1	_	>48	_	
2	t-BuOOH	48	_	
3	NaClO ₂	48	_	
4	H_2O_2	48	40	
5	O ₂	48	53	
6	NaClO	48	85	
7	NaClO	24	85	
8	NaClO	20	85	
9	NaClO	15	85	
10	NaClO	10	85	
11	NaClO	8	80	
12	NaClO	5	72	
13	NaClO	1	64	
14	NaClO ^c	10	85	
15	NaClO ^d	10	85	
16	NaClO ^e	10	85	
17	NaClO ^f	10	70	

Effect of the oxidants on C-H oxidation of ethyl benzene.^a

^a Reaction condition: a solution of the [Gmim]Cl-Cu(II) (0.1 mmol), ethyl benzene (2 mmol) and different oxidants (2 mmol) at ambient temperature.

^b Yield determined by HPLC.

^c 10 mmol NaClO was used.

^d 5 mmol NaClO was used.

^e 2 mmol NaClO was used.

f 1 mmol NaClO was used.

Table 1

Entry	Catalyst (mmol)	Time (h)	Conversion ^b (%)	Yield ^f (%)	
1	_	48	Trace	Trace	
2	[Gmim]Cl ^c	24	37	34	
3	CuCl ₂	24	30	26	
4	CuCl ₂ /[Gmim]Cl	24	51	48	
5	[Gmim]Cl-Cu(II)	10	89	85	
6	[Gmim]Cl-Cu(II) ^d	10	90	86	
7	[Gmim]Cl–Cu(II) ^e	8	90	87	
8	[Gmim]Cl–Cu(II)	11	89	86	

Table 2 Optimization of the [Gmim]Cl–Cu(II) complex catalyzed C–H oxidation of ethyl benzene.^a

^a Reaction condition: a solution of the catalyst (0.1 mmol), ethyl benzene (2 mmol), NaClO (2 mmol) at ambient temperature. ^b Determined by HPLC.

^c 1-Glycyl-3-methyl imidazolium chloride ionic liquid.

^d 0.2 mmol [Gmim]Cl–Cu(II) complex was used.

^e Reaction was carried out at 60 °C.

^f Isolated yield by flash chromatography.

Next, we have screened a number of different catalysts on the model reaction. At first, the oxidation reaction was unsuccessful in absence of catalyst (Table 2, entry 1). Furthermore; the reaction was carried out in the presence of [Gmim]Cl, CuCl₂, CuCl₂/[Gmim]Cl with different intervals, it gave 34–48% of carbonyl compounds (Table 3, entries 2–4). Finally, desired product was obtained in the presence of [Gmim]Cl–Cu(II), which have higher yield (Table 2, entry 5). Moreover, the reaction was not accelerated obviously inspite of increased the amount of catalyst from 0.1 to 0.2 mmol (Table 2, entry 6). Almost similar yield was obtained when slightly increasing the temperature (60 °C) and duration of the reaction (Table 2, entries 7 and 8).

Having optimized the reaction conditions, the oxidation of different alkyl-arenes and cyclohexane were examined (Table 3). The oxidation of ethyl benzene and *n*-butyl benzene afforded the corresponding ketones with 85 and 82% yield (Table 3, entries 1 and 2). As it could be expected, higher conversion (88%) was also obtained with diphenylmethane (Table 3, entry 3). Treatment of 3-phenyl-1-propanol with NaClO in [Gmim]Cl–Cu(II) complex system afforded the corresponding 2-benzoyl ethanol with 82% yield (Table 3, entry 4).

In the case of acetate as substrate for this reaction, modulator desired product were detected (Table 3, entries 5 and 6). Further, this optimized condition applied in alicyclic system with [Gmim]Cl–Cu(II) complex with 70 and 88% yields (Table 3, entries 7 and 8).

Subsequently, the recyclability of the used complex was demonstrated for the oxidation of ethyl benzene to acetophenone. The catalytic system could be reused directly for the next cycle, after full extraction of the product $(3 \times 5 \text{ mL})$ diethyl ether per extraction and drying in *vacuo*. The results shown in Table 4 demonstrate that this oxidative system was readily recyclable for seven runs without any significant loss of catalytic activity (Table 4).

Entry	Substrate	Time (h)	Product ^b	Yield ^c (%)	Boling point (°C)	
1	Ethylbenzene	10	Acetophenone	85	202	
2	<i>n</i> -Butylbenzene	11	Butyrophenone	82	228-230	
3	Diphenylmethane	11	Benzophenone	88	47 ^d	
4	3-Phenyl-1-propanol	10	2-Benzoyl ethanol	82	289	
5	3-Phenylpropyl acetate	10	2-Benzoylethyl acetate	80	306	
6	4-Phenylbutyl acetate	12	3-Benzoyl propyl acetate	80	326	
7	Cyclohexane	12	Cyclohexanone	70	155	
8	1,2,3,4-Tetrahydronaphthalene	12	α-Tetralone	88	113	

Benzylic C-H oxidation	of alkyl-arenes using	[Gmim]Cl-Cu(II)	ionic liquid at a	mbient temperature. ^a
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^a Reaction condition: a solution of the catalyst (0.1 mmol), ethyl benzene (2 mmol), NaClO (2 mmol) was stirred at ambient temperature.

^b All the products were characterized by spectroscopic analysis (IR, MS, ¹H NMR, melting/boiling point) known compounds were compared with authentic data.

^c Isolated yield by flash chromatography.

^d Melting point.

Table 3

Table 4 Catalyst recyclability studies in oxidation of ethylbenzene at room temperature.^a

Cycles	1	2	3	4	5	6	7
Yields ^b	85	85	83	83	83	82	80

^a Reaction condition: a solution of the catalyst (0.1 mmol), ethylbenzene (2 mmol), NaClO (2 mmol) at ambient temperature.

^b Isolated yield by flash chromatography.

In summary, we have successfully developed a novel, practical and eco-friendly method for the oxidation of alkylarenes and cyclohexane by using [Gmim]Cl–Cu(II) complex at 25 °C under solvent-free condition. In addition, this methodology offers a competitive recyclability of the catalyst without a significant loss of its catalytic activity and the catalyst could be readily reused, thus making this procedure more environmentally acceptable whilst no catalyst leaching was observed. Further investigation on the application of this kind of supported catalyst is still underway in our laboratory.

2. Experimental

The catalyst [Gmim]Cl–Cu(II) was synthesized according to literature [17] and structure conformation is available in supplementary report.

2.1. Typical procedure for oxidation of alkenes

A solution of the alkane (2 mmol), Cu(II) complex (0.1 mmol) and NaClO (2 mmol) was stirred at 25 °C for the appropriate time (see Table 3). After the completion of the oxidation, the mixture was extracted with diethyl ether (3×5 mL). The combined ether phase was concentrated in *vacuo* and monitored by HPLC and ¹H NMR. Then the residue was purified by flash chromatography (ethyl acetate/chloroform = 0.5:4.5 mL) to afford corresponding ketones in 70–88% yields. The spectral data of the various ketones were found to be satisfactory in accord with the literature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2012.04.014.

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