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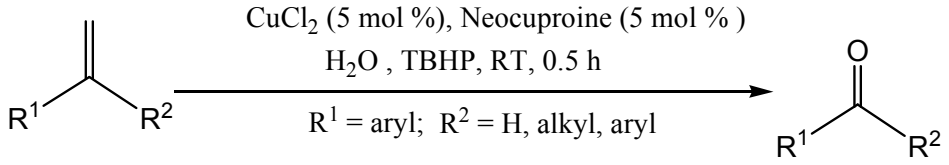
Efficient and selective copper-catalyzed organic solvent-free and biphasic oxidation of aromatic *gem*-disubstituted alkenes to carbonyl compounds by *tert*-butyl hydroperoxide at room temperature

Md. Munkir Hossain,[a] Wei-Kai Huang,[a, b] Hung-Jie chen,[a, c] Pei-Han Wang[a, c] and Shin-Guang Shyu[*a]

Biphasic Cu(II) catalyzed selective oxidative cleavage of aromatic *gem*-disubstituted alkenes to carbonyl compounds using *tert*-butyl hydroperoxide at room temperature.



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Copper-catalyzed alkene oxidation to carbonyl compounds by *tert*-butyl hydroperoxide (TBHP) under organic solvent-free and biphasic conditions at room temperature is selective for aromatic *gem*-disubstituted alkenes. Enhanced reactivity was observed in the presence of 2,9-dimethyl-1,10-phenanthroline (neocuproine). The reaction is economically attractive because the yield is high, and separation of products and recycling of the catalyst are easy.

Oxidative alkene cleavage is an important synthesis method because besides introducing oxygen functionalities, the C=C cleavage can selectively split large molecules and remove protecting groups.[1] Enzymatic cleavage of alkene double bonds under O_2 in aqueous buffer at room temperature is reported[2] and that, in certain cases, occurs in a high chemo- and regioselective fashion. However, the reaction requires long reaction time and is not *via* a simple operation protocols.[3] On the other hand, among chemical methods, ozonolysis is a classical one[4] but its application is often limited due to safety concerns.[5] Besides ozonolysis, both metal (such as Ru,[6] Os,[7] W,[8] Re,[9] Pd,[10] Fe,[11] and Au[12]) and metal free (aryl-λ^3-iodane-based)[13] methods were developed to catalyze the oxidative cleavage reaction. Despite the substantial progress made in the chemical oxidative cleavage of alkenes, green processes are scarce.

Solvent-free reaction is the best solvent system in green chemistry. However, if solvent is unavoidable, water instead of organic solvent is considered. Water is a green solvent not only because it is environmentally benign, non-toxic, non-flammable and abundantly available but also able to exhibit different reactivity in comparison to organic solvents.[14] Reactions in water can enhance the reaction rate and the selectivity of reactants having low solubility owing to their hydrophobic effect.[14c] Water also has an advantage of separation over organic solvents where products are hydrophobic and the catalyst is soluble in water. Oxidation reactions *in vivo* are in an aqueous environment. Thus, the development of a biomimetic catalytic system which is stable and operates in aqueous medium is highly desirable.

Use of copper salts or complexes as the catalysts has gained much prominence recently because of their viability, reduced handling hazard, good functional group tolerance and scalability in synthetic procedures. Copper is involved in the cleavage of different types of C–C single bonds,[15] C=C double bonds in ketenimines[16] and aromatic enol ethers,[17] C≡C triple bond in *O*-propargyl oximes[18] and aromatic ring cleavage in catechol.[19] Although *in vivo*[1a] and electrochemical[20] oxidative cleavage of the C=C double bond in oxygen involving copper have been reported,[21] oxidative cleavage of alkenes to carbonyl compounds using copper salts or complexes is rare.[21] Herein we report a selective and efficient oxidation of terminal alkenes to their corresponding carbonyl compounds catalyzed by Cu(II) salts with and without ligands using *tert*-butyl hydroperoxide (TBHP) as an oxidant at room temperature under organic solvent-free and biphasic condition.

The alkene 1,1-diphenylethylene was used as the model substrate. Water soluble $[Cu(\mu\text{-}Cl)Cl(phen)]_2$ (**1**), which can be synthesized in high yield via a simple method,[22] catalyzes the oxidative cleavage reaction with 81% yield in 24 hours. Oxidation using $CuCl_2{\cdot}2H_2O$ instead of **1** produced similar results. We have then optimized the yield with different copper salts, oxidants, and ligands in different solvents under the same condition. The results are summarized in Table 1.

Among different bidentate nitrogen containing ligands (Table 1, entries 1,2,4,5), 2,9-dimethyl-1,10-phenanthroline (neocuproine) can complete the cleavage reaction in half an hour in the presence of

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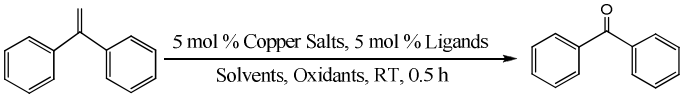
†Electronic supplementary information (ESI) available: Experimental details, copies of NMR and GC spectra. See DIO: 10.1039/c3gc….

$CuCl_2·2H_2O$ and water (Table 1, entry 2); whereas the reaction without ligand requires a longer time (20 hours) under identical condition (Table 1, entry 6).

Table 1 Optimization of the reaction condition for oxidative cleavage of 1,1-diphenylethylene in different solvents, copper salts, oxidants, and ligands[a]



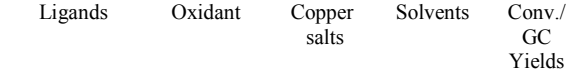
Entry	Ligands	Oxidant	Copper salts	Solvents	Conv./ GC Yields
1	Phen[b]	TBHP	$CuCl_2$	H_2O	21/13
2	Neocuproine	TBHP	$CuCl_2$	H_2O	99/81
3[c]	Neocuproine	TBHP	$CuCl_2$	H_2O	–
4	Bipyridine	TBHP	$CuCl_2$	H_2O	30/21
5	DMB[d]	TBHP	$CuCl_2$	H_2O	25/14
6	No ligand	TBHP	$CuCl_2$	H_2O	25/17[e]
7	Neocuproine	TBHP	$CuBr_2$	H_2O	100/81
8	Neocuproine	TBHP	CuCl	H_2O	100/82
9	Neocuproine	TBHP	CuBr	H_2O	100/81
10	Neocuproine	TBHP	$Cu(NO)_3$	H_2O	70/51
11	Neocuproine	TBHP	$CuCl_2$	CH_3CN	100/78
12	Neocuproine	TBHP	$CuCl_2$	CH_2Cl_2	100/82
13	Neocuproine	TBHP	$CuCl_2$	Me_3COH	100/81
14	Neocuproine	TBHP	$CuCl_2$	Pentane	100/83
15	Neocuproine	H_2O_2	$CuCl_2$	H_2O	Trace
16	Neocuproine	THFHP[f]	$CuCl_2$	H_2O	65/53
17	Neocuproine	CHP[g]	$CuCl_2$	H_2O	100/87
18	Neocuproine	TBHP	$CuCl_2$[h]	No	100/84
19	Neocuproine	TBHP[i]	$CuCl_2$[h]	No	100/95
20[c]	Neocuproine	TBHP[i]	$CuCl_2$[h]	No	Trace
21	Neocuproine	TBHP	No	H_2O	Trace
22	Neocuproine	TBHP	No	No	Trace
23	Neocuproine	TBHP[i]	No	No	Trace

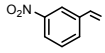
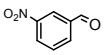
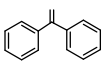
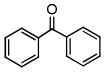
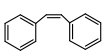
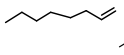
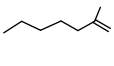
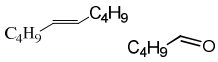
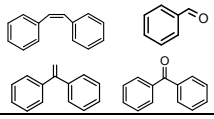
[a] Reaction conditions: alkene (0.2 mmol). ligand (0.01 mmol). Cu salt (0.01 mmol, in aqueous solution). *tert*-butyl hydroperoxide (1.55 mmol, 70% aqueous solution). H_2O (0.7 mL). [b] phenanthroline. [c] add 2,6-di-*tert*-butyl-4-methylphenol (2 mmol). [d] 4,4'-dimethyl-2,2'-bipyridine. [e] reaction completed after 20 h with 78 % yield. [f]THF-hydroperoxide. [g] cumene hydroperoxide. [h] solid $CuCl_2·2H_2O$ (0.01 mmol). [i]TBHP (1.5 mmol, 5M-6M decane solution).

Copper catalyzes the reaction because when copper is absent, only trace amount of cleavage product benzophenone is obtained (Table 1, entries 21-23). Both Cu(I) (Table 1, entries 8-9) and Cu(II) halides gave almost identical results which indicates that they may have similar active species in the reactions. The active specie or species should be Cu(II) moieties because the reaction is under oxidation condition. Irrespective of the copper oxidation state, copper halide salts are more effective to cleave the alkene double bond (Table 1, entries 2, 7-10) in comparison with that of the nitrate salt (Table 1, entry 10) with neocuproine in aqueous medium (organic-solvent free). For organic solvents, both polar and non-polar solvents are equally effective in the cleavage reactions (Table 1, entries 11-14) when $CuCl_2·2H_2O$ and neocuproine were used.

Regarding oxidant, H_2O_2 is not active (Table 1, entry 15). Among organic peroxides, 2-hydroperoxytetrahydrofuran (THFHP) is less active as compared to *tert*-butyl hydroperoxide (TBHP) and cumene

Table 2 Oxidative cleavage of alkenes into aldehydes and ketones in organic-solvent free and biphasic conditions [a]



Entry	Alkenes	Products	Yield [b] %/Selectivity [c]% A[d]	B[e] □ B[f]
1			43(37) /43	25[g]/41 □ 17/20[h]
2			30(24)/30	21[i]/38 □ 12/12
3			29 (23)/29	7[j]/47 □ 12/12
4			78/78	87(87)/87 □ 95/96
5			81/81	96(91)/96□ 99/99
6			82/82	91(89)/91 □ 84/85
7			79/79	89(86)/89 □ 93/94
8			80/80	98(92)/98 □ 93/94
9			17[k]/30	trace □ 10/28[l]
10			–[m]	–
11			–	–
12			–	–
13			Trace 88/88	Trace□Trace 89/89□84/86[n]

[a] Reaction conditions: alkene (0.2 mmol). *tert*-butyl hydroperoxide (1.55 mmol). $CuCl_2·2H_2O$ (0.01 mmol). [b] GC yield using internal standard 1,4-di-*tert*-butylbenzene; isolated yield in the parenthesis. Both are based on 100 % conversion. [c] based on GC yield and 100% conversion. [d] 5 mol% $CuCl_2·2H_2O$ (0.01 mmol, in H_2O), H_2O (0.7 mL), reaction time 20 h. [e] 5 mol% $CuCl_2·2H_2O$ (0.01 mmol, in H_2O) + 5 mol% neocuproine (0.01 mmol), H_2O (0.7 mL), reaction time 0.5 h. [f] 5 mol% $CuCl_2·2H_2O$ (0.01 mmol, solid) + 5 mol% neocuproine (0.01 mmol), TBHP in decane solution (1.5 mmol), reaction time 0.5 h.[g] 60% conversion. [h]83% conversion.[i] 56% conversion. [j] 15% conversion. [k] 57% conversion. [l]55% conversion. [m] no reaction. [n]98% conversion.

hydroperoxide (CHP) (Table 1, entries 2, 16 and 17). Thus the order of reactivity is TBHP ~ CHP > THFHP > H_2O_2. The positive inductive effect of methyl substituent of organic peroxides may facilitate the formation and stabilization of free radicals (the usual reaction intermediate generated during oxidation by peroxide) to interact with the substrates for their quick conversion.

The Cu(II) catalytic systems **A** ($CuCl_2 \cdot 2H_2O$) and **B** ($CuCl_2 \cdot 2H_2O$ + neocuproine) were applied to various alkenes. The results are summarized in Table 2. For the case of aromatic *gem*-disubstituted alkenes, catalytic system **B** (with neocuproine) afforded higher selectivity and reactivity than **A** (without neocuproine) as the reactions completed in half an hour for **B** (with high yield) vs 20 hours for **A** (with less yield compared to **B**) under identical condition (Table 2, entries 4-8).

The reason that neocuproine (2,9-dimethyl-1,10-phenanthroline) can enhance the reactivity of the cleavage reaction as compared to the reactions with other ligands (Table 1, entries 1,4,5) or without ligand (Table 2, entries 4-8 with catalyst **A**) is not clear. Reactivity enhancement due to inductive effect of methyl substituent should be minor as the ligand 4,4'-dimethyl-2,2'-bipyridine with methyl substituent shows a low reactivity (Table 1 entry 5). The steric hindrance due to the methyl substituent in the ligand which is considered to be a cause of reactivity difference between a non-substituted bidentate ligand and a substituted ligand may be the reason (Chart 1).[23] A combination of neocuproine and a π-acceptor alkene may stabilize the unusual coordination geometry leading to a tunable control of the cleavage reaction.[24]

Chart 1

Oxidative cleavage occurred with similar efficiency for α-methyl styrene and its derivatives with either electron-donating or electron-withdrawing substituents at the para position of the phenyl ring (Table 2, entries 5-8). Moreover, the aromatic mono-substituted alkenes are less selective (Table 2, entries 1-3) irrespective of electronically neutral (Table 2, entry 1), rich (Table 2, entry 2), or poor (Table 2, entry 3) substituents. The above reactivities for both aromatic *gem*-disubstituted and mono-substituted alkenes indicate that the electronic effect of the substituents does not affect the rate of their oxidation. Aliphatic *gem*-disubstituted (Table 2, entry 11), mono-substituted (Table 2, entry 10) and internal alkene (Table 2, entry 12) are inert towards the oxidative cleavage of their double bonds.

Internal aromatic alkenes are much less reactive than terminal aromatic alkenes (Table 2, entries 9 and 4). This reactivity difference was demonstrated by the reaction of mixed equimolar amounts of terminal 1,1-diphenylethylene and internal *cis*-stilbene which led much higher yield of 1,1-diphenylethylene to benzophenone (Table 2, entry 13). The reaction was monitored by GC. Conversion of 1,1-diphenylethylene to benzophenone was fast (initiated within a minute, Fig. **1a**, and completed in half an hour, Fig. **1b**) as compared to that of *cis*-stilbene to benzaldehyde (trace in half an hour, Fig. **1b**). Although regioselective oxidation of alkenes to epoxides is known,[25] examples of regioselective cleavage of alkene is rare.[26] The observed selectivity in Table 2 may be useful in synthetic organic chemistry when there are different types of double bonds in the same substrate.

The Cu(II) catalyst remained its activity through the end of the reaction because we observed further conversion of alkene to the corresponding ketone when additional alkene (e.g., 1,1-diphenylethylene) and TBHP were added to the aqueous layer containing the dissolved catalyst (the product benzophenone was transferred to the organic layer leaving soluble copper catalyst in water when ethyl acetate was added into the reaction mixture under stirring) Fig. 2. The reaction was repeated ten times with similar activity using the same separated catalyst (see the Supporting Information Fig. S17).

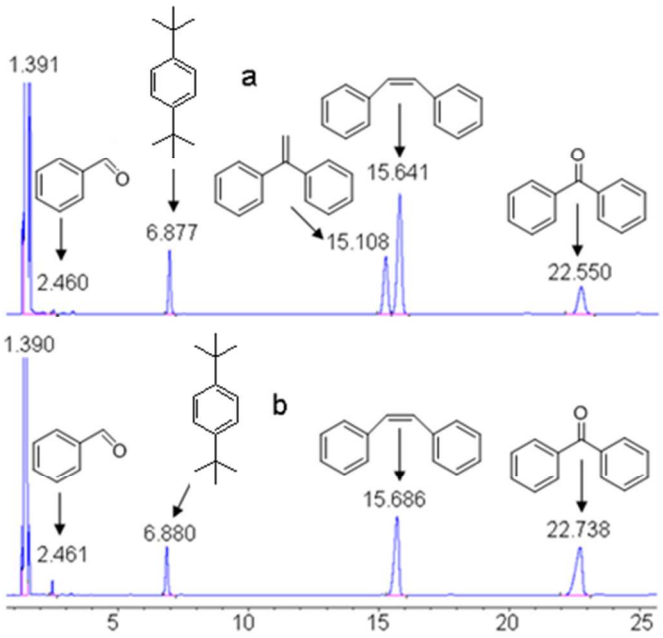


Fig. 1 (a) GC spectrum of the reaction mixture within 5 minutes (b) GC spectrum of the reaction mixture after half an hour.

Use of peroxides for alkene oxidation, in particular H_2O_2, is mostly limited to epoxidation,[27] and carboxylic acid formation (an over oxidation product).[11,28] Selective oxidative cleavage of alkene to carbonyl compounds is scarce.[26,29] On the other hand, most of the reported chemical methods for the alkene cleavage suffer from limitations of toxicity, long reaction time, harsh reaction conditions,

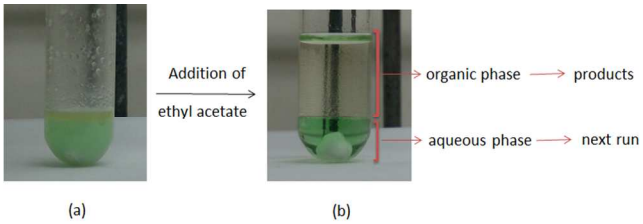
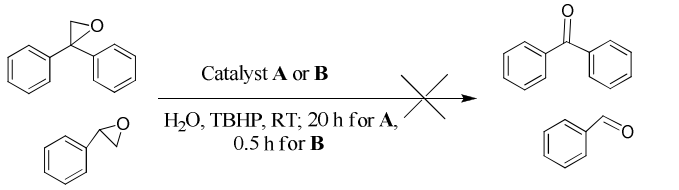


Fig. 2 (a) Reaction mixture in water (b) organic phase containing products and the aqueous phase including copper catalyst after adding ethyl acetate

tedious workup or low product selectivity.[4-9] Alkene cleavage reactions catalyzed by inexpensive and nonhazardous catalysts using oxygen or H_2O_2 (35 wt. % aqueous solution) as oxidants in H_2O at room temperature are usually considered green. Nowadays readily available 70% aqueous TBHP is used frequently as an alternate to H_2O_2 in combination with various metal catalysts.[30] Thus, we consider the method described in this communication is a green one.

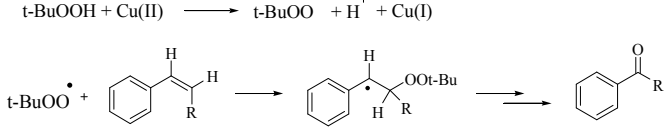
To accumulate more insights about the role of water, we performed reaction without addition of extra water other than water from the source of TBHP (as it is 70% aqueous in solution) (Table 1, entry 18) and used solid $CuCl_2{\cdot}2H_2O$. In addition, we used TBHP decane solution (pure TBHP is not available) and solid $CuCl_2{\cdot}2H_2O$ for the water-free reaction (Table 1, entry 19). The reactions are smooth both in aqueous TBHP with water as the medium (organic-solvent free) and TBHP decane solution without using water as solvent, and yields and selectivities for the case of decane TBHP are similar to that of the aqueous TBHP for different alkenes (Table 1, entries 18 and 19; Table 2, entries 4-9, 13). These observations indicate that the reaction can be carried out in organic solvent (decane in the TBPH decane solution is an organic solvent), and oxidative cleavage of alkene in aqueous medium proceeds in the organic phase—a biphasic reaction. This biphasic concept can also apply to the reactions in both polar and non-polar organic solvents (Table 1, entries 11-14) when aqueous TBHP solution was used. Because water is unavoidable in products separation for further use of the separated catalyst, it has advantages for using the biphasic system (aqueous medium).

When Cu(II) is absent, we only obtained trace amount of product (Table 1, entries 21-23). Oxidative cleavage of alkenes by hydroperoxides is generally proceeded through a free radical pathway.[31] For metal ion catalyzed hydroperoxy reactions, the most important function of the catalyst is the decomposition of relatively stable hydroperoxides into radicals.[31] Addition of radical scavenger 2,6-di-*tert*-butyl-4-methylphenol in our system inhibited the cleavage reaction indicating the presence of free radical pathway (Table 1 entries 3 and 20). All these indicates that one major function of Cu(II) is to decompose the peroxide into radicals.[31] Alkene cleavages through the epoxide as an intermediate may not be the reaction path as the control oxidation of styrene epoxide and 1,1-diphenylethylene oxide not afforded the respective carbonyl compounds in identical reaction conditions (eq. 1).[32] Based on the above observations, we proposes the reaction paths of the reaction as shown in Scheme 1.



(1)

Scheme 1



In conclusions, we report a simple, efficient, and green catalyst system for the oxidative carbon–carbon double bond cleavage reaction. The catalyst in our study can be considered as a biomimetic catalyst with short reaction time and simple operation protocols. The catalyst can be recycled for ten times without losing activity. The product can be separated by extraction with organic solvent, and the catalyst remains dissolved in the aqueous layer for further use.

Acknowledgments

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