Visible Light-Mediated Copper(I)-Catalysed Aerobic Oxidation of Ynamides/Ynamines at Room Temperature: A Sustainable Approach to the Synthesis of α-Ketoimides/α-Ketoamides

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Abstract: A novel visible light-mediated, coppercatalysed aerobic oxidation of the C=C bond in ynamides/ynamines at room temperature by using molecular oxygen as an oxidant is described. Overall, 23 examples were demonstrated with substrates having a wide range of functional groups. The current protocol can be readily scaled up to a preparative (1-2 g) scale with high yields (78-92%), high atom efficiency, and reaction mass efficiency. The mechanistic study shows that in-situ formation of a copper(I)-coordinated π -complex ($\lambda_{max} = 460 \text{ nm}$) is most probably the key light absorbing species responsible for the visible light-induced oxidation of ynamides and ynamines. This sustainable oxidation approach allows the direct synthesis of potentially important novel α -ketoimide/ α -ketoamide skeletons without the need of external oxidants (organic/inorganic oxidants) and generation of stoichiometric amounts of wastes.

Keywords: copper; molecular oxygen; oxidation; photochemistry; radicals

Molecular oxygen-promoted oxidation of hydrocarbon and heteroatom-containing organic compounds under mild conditions (room temperature) has recently emerged as an efficient and sustainable synthetic approach for the construction of synthetically and biologically potent molecules.^[11] In this regard, oxidation of C=C triple bonds is one of the unique oxidation process^[2] for the preparation of 1,2-diketone derivatives, and thus many powerful transition metalcatalysed processes have been reported.^[3] Heteroatom-substituted alkynes, such as ynamides, are structurally very special,^[4] and are involved in many transformations including cycloaddition and other reactions, producing a diverse array of heterocyclic compounds.^[5] Consequently, oxidation of the C=C bond of ynamides is receiving much attention and represents one of the most straightforward methods for a direct access to potentially important synthons, such as, α -ketoimides.^[6] α -Ketoimides are structurally similar to α -ketoamides^[7] and are important building blocks in organic synthesis.^[6] Their derivatives are privileged precursors for diversified natural products of pharmacological importance.^[8] Conventionally, αketoimides can be synthesized by direct amidation of activated carbonyl groups.^[6b,9] But these methods often require pre-synthesized carbonyl reagents. Only very few examples have been reported for the oxidation of ynamides by using a ruthenium or gold catalyst in the presence of organic oxidants (up to 3.0 equivalents) at high temperatures for the preparation of α -ketoimides.^[10] Despite the efficient oxidation processes, common disadvantages have also been observed, such as (i) usage of stoichiometric strong oxidants (organic/inorganic oxidants), thus leading to the generation of stoichiometric amounts of undesired wastes, (ii) usage of expensive metal catalysts, and (iii) typically the reactions are performed at high temperatures.

Thus, it is highly desirable and challenging to develop an environmentally benign and operationally simple method for the preparation of novel α -ketoimide/ α -ketoamide skeleton through the direct aerobic oxidation of ynamides/ynamines by using the inexpensive simple CuCl salt as a catalyst without the need of external oxidants under low energy visible light irradiation, which would be of value in organic synthesis. From an ecological point of view, using molecular oxygen as an oxidant represents one of the most efficient and atom-economical transformations.^[1] Visible light activated photoredox catalysis is being

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accepted as a powerful and green alternative to metal-catalysed thermal reactions.^[11] Indeed, visible light is an environmentally friendly and sustainable source of energy for functional group transformations.^[11d] Most of visible light-mediated reactions are typically performed at room temperature in the absence of ligands or additives. Moreover, visible light is easier to handle than high energy harmful UV light; reagents and products, including complex organic molecules, are more stable under low energy visible light irradiation conditions. Inexpensive, photoredox copper catalysis has been studied in various coupling reactions, such as, C-C cross-coupling, and various C-N, C-S and C-O cross-coupling reactions.^[12] In connection to copper photoredox catalysis, previously we reported several examples of visible light-mediated CuCl-catalysed efficient C-C, C-N cross-coupling, and C–H annulation reactions.^[13]

Herein, we report a novel and effective aerobic oxidation of ynamides/ynamines for the prepration of α ketoimides/α-ketoamides under the combination of CuCl and low energy visible light irradiation (Scheme 1, current work). The current oxidation process is unprecedented, and is complementary to our previous work on oxidative C-N coupling of anilines and terminal alkynes for the preparation of ketoamides^[13c] because, in that work the highly electron-rich ynamine intermediates (highly unstable) cannot be isolated. However, the current work deals with oxidation of the C=C triple bonds of ynamides as well as stable ynamines. Based on our previous work,^[13c] Cu(I) ion could coordinate to the C=C bond of ynamides to form a Cu(I) π -complex, which can further undergo reactions with O_2 to generate the desired α ketoimides upon visible light irradiation. Importantly, oxidation of the C=C bond of ynamides is much more difficult than that of the C=C in ynamines,^[4b,10b] since ynamides have less π -basicity on the C=C triple bond and thus favor the oxidation reaction using soft Lewis



Scheme 1. Transition metal-catalysed oxidation of ynamides.

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acid^[14] such as Cu(I) upon photo irradiation. However, the same reaction does not occur under thermal conditions, even when heated to high temperatures.^[10a,12c] Photo-excitation can provide sufficient electronic excitation energy for the ground state Cu(I) π -complex to overcome an energy barrier. Subsequent dark reaction with molecular oxygen can form a copper peroxo complex and initiate the oxidation of the C=C bond of ynamides (see, details in the mechanism discussion below).

The significance of the present chemistry includes: (i) this is the first example that CuCl-catalysed oxidation of ynamides/ynamines to α -ketoimides and α -ketoamides at room temperature; (ii) molecular oxygen (O₂) was used as an oxidant, and (iii) a mechanistic investigation illustrates that *in-situ* formation of a Cu(I)-coordinated π -complex might be the key catalyst responsible for the oxidation of ynamides/ynamines to α -ketoimides and α -ketoamides.

The oxidation reaction of ynamide (1a) was chosen as the model substrate for optimisation of the experimental parameters. In an initial study (see Table 1), we were delighted to find that oxidation the C=Cbond of ynamide (1a) in acetonitrile in the presence of 5 mol% CuCl and molecular oxygen (1 atm) at room temperature under blue LEDs irradiation (10 h) furnished the corresponding α -ketoimide in 93% yield (Table 1, entry 1). Different solvents were examined for oxidation of ynamide (1a). However, acetonitrile was found to be the best solvent, in which the highest yield of 93% was obtained, whereas moderate to low yields were obtained when using other solvents (see entries 4-7). Addition of 0.5 mL water to the reaction mixture does not affect the product yield (entry 8). In the catalytic screening, CuX (X = Cl, Br) affords the highest yield of the oxidation product. CuCl₂ as catalyst could also produce the oxidation product, but fails to give high yields (entry 3). Control experiments reveal that exclusion of either light, Cu catalyst, or O₂, results in no oxidation reaction (entries 10-12).

Under the optimized conditions, (Table 1, entry 1), we then explored the substrate scope of ynamides containing various arylamine, alkynes and tosyl derivatives (see Table 2). In the oxidation reaction, both electron-rich, electron-neutral and electron-poor group-substituted arylamines on the C=C bond of ynamides underwent oxidation smoothly to afford the corresponding α -ketoimide products (**2a–2d** and **2g–2h**, 89 to 93% and 78–80% yields, respectively). Notably, the current oxidation reaction also works well for halide-substituted arylamines in the ynamide moiety (X=Br and I), and affords their α -ketoimide products with 82–85% yields (**2e** and **f**). Importantly, this halo-substituted group in α -ketoimides is useful for further synthetic modifications.^[15]

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Table 1. Optimization of the reaction conditions.^[a]



Entry	[Cu] Catalyst	Solvent	Yield [%] ^[b]
1	CuCl	CH ₃ CN	93
2	CuBr	CH ₃ CN	92
3	CuCl ₂	CH ₃ CN	76
4	CuCl	CH ₃ CN/CH ₃ OH	86
5	CuCl	CH ₃ OH	72
6	CuCl	DMF	54
7	CuCl	THF	48
8 ^[c]	CuCl	CH ₃ CN/H ₂ O	88
9 ^[d]	CuCl	CH ₃ CN	82
10 ^[e]	CuCl	CH ₃ CN	trace
11 ^[f]	CuCl	CH ₃ CN	n.r
12 ^[g]	CuCl	CH ₃ CN	trace
13 ^[h]	CuCl	CH ₃ CN	88

[a] Unless otherwise mentioned, reaction conditions are as follows; 1a (0.5 mmol), 5 mol% of [Cu] catalyst, solvent (7 mL). The mixture was irradiated with blue LEDs (power density: 40 mW cm^{-2} at 460 nm) for 10 h in an O₂ atmosphere (1 atm).

- [b] Yield of the isolated product.
- ^[c] 0.5 mL water was added.
- [d] Irradiation with an ambient white light bulb for 15 h (power density: 8 mW cm^{-2} at 460 nm).
- [e] Reaction was conducted in the dark at 80 °C.
- [f] In the absence of CuCl catalyst.
- [g] In the absence of O_2 .
- [h] 1 atm. air (in a balloon) was used in the reaction.

Next, we further explored the substrate scope of substituted tosyl groups and various alkynes. In most of the cases, substrates with substituted tosyl groups nicely participate in the oxidation reaction to generate the α -ketoimides in 83–89% yields (Table 2, 2p– 2r). The electron-rich phenylacetylene-substituted ynamides (1i, 2j and 1n) can also undergo similar oxidation reaction to afford the corresponding a-ketoimide products (2i, 2j and 2n) in good yields (86-88%). Moreover, it was found that the current protocol can well tolerate an electron-withdrawing phenylacetylene ring in the oxidation of ynamides to produce their corresponding α -ketoimides (2k-2m, 8083% yields) within a period of 15–17 h. Aliphatic linear alkynes in the ynamides can also be readily oxidized and converted to the α -ketoimide (20) in 85% vield without affecting the aliphatic chain. Finally, the 4-bromo-substituted tosyl group as well as 4-ester-substituted arylalkyne groups in the ynamide moieties can readily undergo the oxidation reaction and afford the α -ketoimide **2r** in 83%. Thus, the ynamide oxidation reaction works well for a wide range of functional groups, such as, alkoxy, halo, cyano, ester, and naphthyl, and is a powerful method for for the synthesis of α -ketoimides using O₂ as oxidant.

After investigation of N-tosyl- and alkyne groupsubstituted ynamides, the scope of carbazole-type ynamines was also explored for the same oxidation reaction (see Table 3). We observed that carbazole-substituted ynamines can be easily converted into their corresponding α -ketoamides (4a-4e) with 82-89% yields upon blue-LEDs irradiation in the presence of O_2 and 5 mol% CuCl (see Table 3). Certainly, carbazole derivatives are an important scaffold in natural products and medicines.^[16] It is worthy to note that as compared to N-tosyl group-substituted ynamides, carbazole-bearing ynamines readily undergo the oxidation reaction within short periods of time (7–10 h). This is due to the fact that CuCl could easily coordinate with the C=C bond of ynamines. These results provide a key piece of mechanistic evidence that the oxidation reaction proceeds through a Cu(I)-coordinated π complex of the ynamides/ynamines. The structures of 2c and 2d were confirmed by single-crystal X-ray diffraction.^[17]

In addition, the current oxidation process can be readily scaled up to a gram scale (1.0 g, 2.88 mmol, 1a) and produce 0.91 grams of 2a (84% yield) after 12 h of irradiation with blue LEDs at room temperature in the presence of O_2 (1 atm, see Scheme S1 in the Supporting Information). We have evaluated the green chemistry metrics^[13e,18] for the synthesis of the α -ketoimides (2a) in a preparative scale (see the Supporting Information, Table S1). Overall, our green process can enable the α -ketoimides (2a) with an E factor of 8.3, 100% atom economy, 84% atom efficiency, and 91% reaction mass efficiency, which are far better than for previously reported Ru-catalysed thermal processes^[9a] (E factor = 32.5, atom economy = 68%, atom efficiency = 62%, reaction mass efficiency=36%, see, Table S2 in the Supporting Information), since the current photochemical process does not require any organic strong oxidants and expensive metal catalysts, and thus is a sustainable and green process for the synthesis of various a-ketoimides/aketoamides (on a large scale).

With respect to the UV-visible absorption spectra, the experimental results, and our previous studies,^[13c,d] a possible reaction mechanism for the visible light-initiated, CuCl-catalysed oxidation of ynamides is pro-

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^[a] Standard conditions; isolated yields after purification by column chromatography on silica gel.

posed in Scheme 2. The first step involves the formation of Cu(I)-coordinated π -complex of ynamide (A), [^{13c,19]} which has an absorption band at 460 nm (see



^[a] Standard conditions; isolated yields after purification by column chromatography on silica gel.

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Figure 1). Furthermore, formation of this Cu(I)-coordinated π -complex of ynamide was confirmed by the detection of heat release upon complexation using isothermal titration calorimetry (ITC) measurements,^[20] which gives an association constant of Ka $\approx 194 \,\mathrm{M^{-1}}$ between Cu(I) and 4-methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (**1a**) (see more details in the Supporting Information, Figure S2).



Scheme 2. Proposed mechanism.

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Figure 1. UV-visible absorption spectra of *in-situ* generated light absorbing Cu(I)-ynamide complex (A) in CH₃CN.

Upon blue LED ($\lambda_{max} = 460 \text{ nm}$) light irradiation, photo-excited Cu(I)-π-complex (B) could readily react with molecular oxygen to form a copper(II) peroxo complex.^[13c,21] Isomerisation rearrangement of the resulting copper(II) peroxo complex (C) generates the copper(I) species (**D**).^[13c,22] Finally, this complex D can undergo transformation into the intermediate (E), accompanied with regeneration of the CuCl catalyst. Subsequent O-O bond cleavage of the intermediate (E) will produce the desired α -ketoimide (2a).^[13c] In the current proposed mechanism, the Cu(I)-coordinated π -complex of the ynamide is the light absorbing photocatalyst (λ_{max} =460 nm) and is complementary to our previous light absorbing photocatalyst, Cu(I)-acetylides ($\lambda_{max} = 460-485 \text{ nm}$).^[13] To prove the source of oxygen and gain more insight about the reaction mechanism, we have performed an ¹⁸O₂ labelling experiment under the standard conditions. 98% purity of ¹⁸O₂ gas, instead of ¹⁶O₂ air, was filled in the reaction system. From the ESI mass, the final product was determined to contain a mixture of ¹⁸O and ¹⁶O products with a ratio of 87.5%:12.5% (see details in the Supporting Information). These results unambiguously indicate that the oxygen atoms in the products mainly originate from the molecular oxygen. The 12.5% ¹⁶O-containing product is most probably formed via a partial ¹⁸O-H₂¹⁶O exchange during the silica gel column purification process.^[23]

In summary, we have successfully developed a novel process using visible light-mediated molecular oxygen-promoted oxidation of ynamides/ynamines using simple CuCl as a catalyst for the preparation of α -ketoimides/ α -ketoamides at room temperature without the need for strong organic oxidants. The current method can be readily scaled up to a preparative (1–2 g) scale with high atom efficiency, and reaction mass efficiency. A mechanistic study illustrates that *in-situ* formation of Cua (I)-coordinated π -complex (λ_{max} =460 nm) is most probably the key light absorbing species responsible for the visible light-induced oxidation of ynamides and ynamines. From an environmental point of view, using inexpensive simple CuCl catalyst, molecular oxygen as oxidant, and reaction under low energy visible-light irradiation, make this process a greener alternative to existing thermal methods for the oxidation of ynamides/ynamines. Further investigation on visible light-mediated CuCl-catalysed processes for oxidation of other internal alkynes/hydrocarbons, and detailed mechanistic elucidation are currently ongoing in our laboratory.

Experimental Section

General Procedure

To a dry test tube (20 mL) containing 5 mol% CuCl was added the ynamide/ynamine (0.5 mmol) dry CH₃CN (7 mL) solution *via* a syringe. The suspension was irradiated with blue LED light (40 mW cm⁻² at 460 nm) at room temperature in the presence of 1 atm oxygen until completion of the reaction (it was monitored by thin layer chromatography). The reaction mixture was diluted with 30% ethyl acetate in hexane, and stirred for 10 min. The mixture was filtered through celite and silica gel pads, and then washed with ethyl acetate. The filtrate was concentrated and purified by flash column chromatography on silica gel (using *n*-hexane and ethyl acetate as eluent) to afford the desired α -keto-imide/ α -ketoamide products.

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 $\label{eq:constraint} \begin{array}{l} \mbox{Visible Light-Mediated Copper(I)-Catalysed Aerobic} \\ \mbox{Oxidation of Ynamides/Ynamines at Room Temperature: A} \\ \mbox{Sustainable Approach to the Synthesis of α-Ketoimides/α-Ketoamides} \end{array}$

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