Selective Oxidations

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Chloroacetate-Promoted Selective Oxidation of Heterobenzylic Methylenes under Copper Catalysis**

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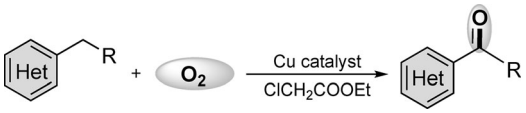
Abstract: *The efficient selective oxidation and functionalization of C–H bonds with molecular oxygen and a copper catalyst to prepare the corresponding ketones was achieved with ethyl chloroacetate as a promoter. In this transformation, various substituted N-heterocyclic compounds were well tolerated. Preliminary mechanistic investigations indicated that organic radical species were involved in the overall process. The N-heterocyclic compounds and ethyl chloroacetate work synergistically to activate C–H bonds in the methylene group, which results in the easy generation of free radical intermediates, thus leading to the corresponding ketones in good yields.*

The direct oxidation and functionalization of C–H bonds under mild conditions is one of the most powerful strategies to construct complex carbonyl compounds.[1] N-heterocyclic ketones represent an important structural motif frequently found in natural products, pharmaceuticals, and agrochemicals.[2] Traditionally, N-heterocyclic ketones are prepared with stoichiometric quantities of a hazardous oxidant.[3] Meanwhile, this process often produces large amounts of unwanted by-products. Besides, transition-metal-catalyzed oxidations of heterobenzylic methylenes with peroxides have also been developed as an efficient approach toward the synthesis of N-heterocyclic ketones.[4,5] Considerable efforts have also been made in the oxidation of C_{sp^3}–H bonds by utilizing catalytic systems without transition metals.[6] More interestingly, recent advances in the selective functionalization of C–H bonds have been achieved with new types of transition metal catalysis.[7] In particular, the direct oxidation and functionalization of C–H bonds with molecular oxygen as the oxidant is still regarded as one of the main challenges for catalysis. Molecular oxygen is a convenient and green oxidant for catalytic chemistry.[8–10] It is important to explore the direct oxidation of C–H bonds with molecular oxygen for the construction of carbonyl compounds in both academic and industrial communities due to its economic and environmentally benign features.[11–14] Recently, the groups of Maes, Miura, and Chiba have reported successful base-metal-catalyzed oxidations of aryl(di)azinylmethanes and indoles with molecular oxygen.[15] In spite of the impressive progress made in this area, the oxidation of aliphatic C–H bonds of N-heterocyclic compounds with molecular oxygen to produce N-heterocyclic ketones is an almost untouched area. Therefore, further research in this area is still warranted.

The key issues of the oxidation of aliphatic C–H bonds of N-heterocyclic compounds that have to be overcome are two significant limitations: a) the coordination between the N-heterocyclic compound and the transition metal; b) the low reactivity of the aliphatic methylene. To solve these problems, we decided to introduce an activating group at the heteroatom to generate the salts of the N-heterocyclic compounds. According to the hypothesis, we take advantage of the interaction between activating group and N-heterocyclic compound to generate the covalent C–N bond. This process would not only decrease the coordination between the substrate and the catalyst, but also activate the C–H bond in the methylene group. Then the aliphatic C–H bond of the N-heterocyclic compound is oxidized with molecular oxygen and the help of a copper catalyst to generate a radical intermediate. Once the N-heterocyclic ketone is formed, the activating group is reduced and removed from the N-heterocyclic compound. Overall, the copper-catalyzed selective oxidation of aliphatic C–H bond of N-heterocyclic compounds promoted by ethyl chloroacetate under mild conditions would be established (Scheme 1). It was important to realize that ethyl chloroacetate is essential for the selective oxidation of the aliphatic C–H bond of N-heterocyclic compounds.

We envisioned that 4-ethylpyridine and ethyl chloroacetate work synergistically to increase the acidity of the hydrogen atoms in the methylene group in polar solvents. DFT calculations showed that the acidity of the methylene



Scheme 1. The copper-catalyzed selective oxidation of N-heterocyclic compounds promoted by ethyl chloroacetate.

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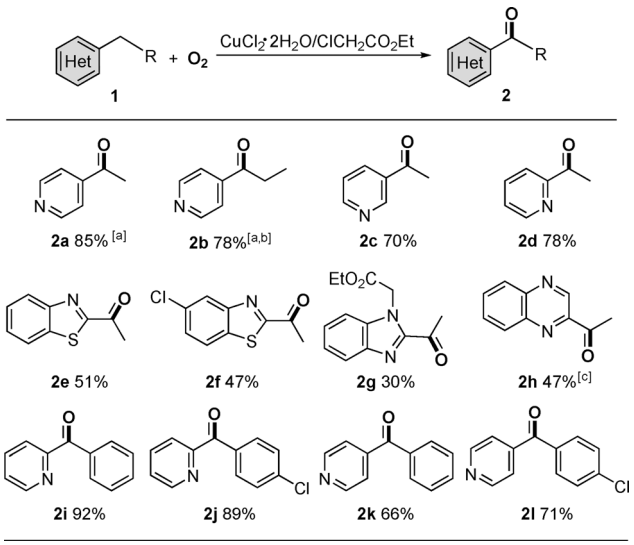
hydrogens of 1-(2-ethoxy-2-oxoethyl)-4-ethylpyridin-1-ium in the gas phase, in dimethylformamide (DMF), and in 1,4-dioxane was largely enhanced compared to the acidity of the methylene hydrogens of 4-ethylpyridine (for more details, see the Supporting Information, SI). These results proved that the formation of a covalent C–N bond increased the acidity of the hydrogen atoms of a methylene group at 4-alkylpyridine and activated the aliphatic C–H bond. To confirm our hypothesis, we investigated the role of ethyl chloroacetate in the oxidation of 4-ethylpyridine (SI, Table S1). Upon examination of the reaction, the formation of a covalent C–N bond was a key factor of activating the aliphatic C–H bond. It was found that ethyl chloroacetate was essential for the oxidation of 4-ethylpyridine to form the desired product (SI, Table S1, entries 1–3). However, little was known about the effect of ethyl chloroacetate in the copper-catalyzed oxidation of benzylic C–H bonds. Based on the above results, a small number of α-halogen compounds was subjected to the oxidation of the aliphatic C–H bond, but no positive results were obtained (SI, Table S1, entries 4–7). Only by using methyl chloroacetate and phenacyl chloride as the activating group, 4-ethylpyridine was selectively oxidized to afford a moderate yield of the desired product. Only traces were obtained when CuI (10 mol%) and HOAc (1.0 equiv) served as the catalyst (SI, Table S1, entry 8). A Brønsted acid could be applied for the activation of pyridines, but the covalent C–N bond formed by HOAc and 4-ethylpyridine was not enough to oxidize the aliphatic C–H bond.

With the optimized conditions in hand, various substituted pyridines were subjected to the copper-catalyzed oxidation of aliphatic C–H bond to test the substrate scope and generality. In the process of optimizing the reaction conditions, we have found that 1,4-dioxane was the best solvent for the oxidation of 4-substituted pyridines, and DMF was the better solvent for all other substrates. As shown in Scheme 2, the reactions proceeded from good to excellent yields in the presence of 4-ethylpyridine, 3-ethylpyridine, and 2-ethylpyridine (**2a**, **2c**, and **2d**). Then we tried to extend the protocol to long-chain aliphatic pyridine. Intriguingly, the 4-propylpyridine was well tolerated and **2b** was obtained in 78% yield. This method was also successfully applied to a variety of 2-ethylbenzo[d]thiazole derivatives, providing the corresponding products in 51% and 47% yields (**2e** and **2f**). It was worth noting that N-heterocycles such as 2-ethyl-1*H*-benzo[d]imidazole and 2-ethylquinoxaline could be applied to the oxidation of aliphatic C–H bonds and gave the corresponding ketones in moderate to good yields (**2g** and **2h**). The reactions of 2-substituted pyridines with typical functional groups such as benzyl and Cl at the 4-position of the benzene ring were successfully employed in the benzylic oxidation (**2i** and **2j**). In addition, 4-substituted pyridines were similarly found to be suitable substrates for the transformation and gave the desired products in excellent yields (**2k** and **2l**).

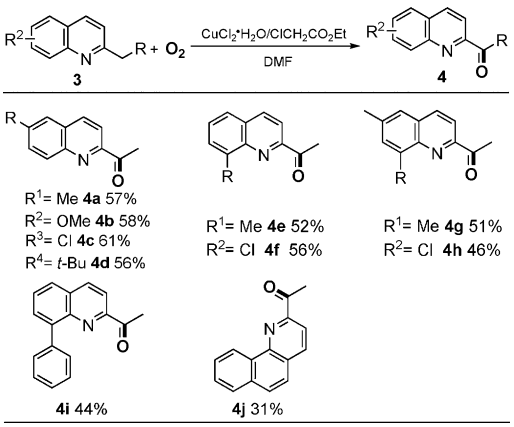
After the successful application of the oxidative reaction of methylene, we tried to extend this process to build up structurally important quinolones. The reaction with 2-substituted quinolines bearing electron-withdrawing and electron-donating groups, such as Cl, Me, MeO, and *tert*-butyl at the 6-position of the benzene ring proceeded



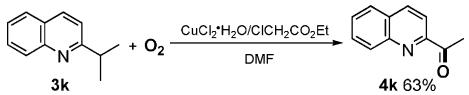
Scheme 2. Copper-catalyzed selective oxidation of the aliphatic C–H bond. Conditions: **1** (1.0 mmol), ethyl chloroacetate (1.0 mmol), $CuCl_2 \cdot 2H_2O$ (10 mol%), DMF (3.0 mL), 130 °C, 24 h, O_2 balloon, yield of isolated product. [a] 1,4-Dioxane (3.0 mL), 100 °C, 24 h. [b] Acetylacetone (10 mol%) was added, and the yield was determined by GC analysis. [c] Ethyl chloroacetate (2.0 equiv).

smoothly to afford the desired products in 56–61% yield (**4a**–**d**; Scheme 3). Furthermore, 2-ethyl-8-methylquinoline and 8-chloro-2-ethylquinoline were also suitable for this reaction (**4e** and **4f**). The methylene group of quinolines with two substituents such as alkyl and chloro were only selectively oxidized to afford the desired products in good yields (**4g**, **4h**). In addition, 2-ethyl-8-phenylquinoline and 3-ethylbenzo[f]quinolone reacted with molecular oxygen under the standard conditions to afford the desired products in moderate yields (**4i**, **4j**). To our surprise, 2-isopropylquinoline could also be utilized to prepare 1-(quinolin-2-yl)ethan-1-one in 63% yield (Scheme 4, **4k**).

To gain insight into the reaction mechanism, we performed a labeling experiment. The reaction between 4-

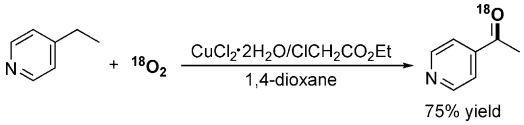


Scheme 3. Copper-catalyzed selective oxidation of the aliphatic C–H bond of 2-substituted quinolines. Conditions: **3** (1.0 mmol), ethyl chloroacetate (1.0 mmol), $CuCl_2 \cdot 2H_2O$ (10 mol%), DMF (3.0 mL), 130 °C, 24 h, O_2 balloon, yield of isolated product.



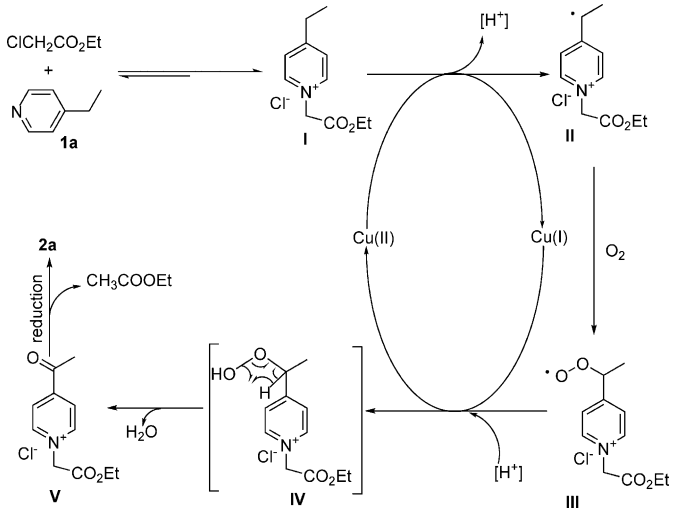
Scheme 4. Copper-catalyzed selective oxidation of 2-isopropylquinoline.

ethylpyridine (**1a**) and ethyl chloroacetate in the presence of $^{18}O_2$ afforded the ^{18}O-labeled product **2a** in 75% yield (Scheme 5), demonstrating that the carbonyl oxygen atom of the 4-acetylpyridine originated from dioxygen as we initially assumed.



Scheme 5. ^{18}O isotope labeling experiment.

When the reaction mixture was investigated by GC-MS, ethyl chloroacetate was found to be converted to ethyl acetate. Based on the above results and previous reports,[9,14] a possible reaction pathway is proposed (Scheme 6). Initially,



Scheme 6. Proposed reaction mechanism.

4-alkylpyridine and ethyl chloroacetate work synergistically to produce 1-(2-ethoxy-2-oxoethyl)-4-alkylpyridin-1-ium chloride. Formation of the pyridinium activates the methylene C–H bonds and intermediate **I** is directly oxidized by Cu^{II} to afford the radical species **II**. As a result, Cu^{I} and H^+ are generated. Subsequently, intermediate **II** easily combines with molecular oxygen to form the peroxy radical species **III**. Then, radical species **III** is reduced by the copper(I) catalyst followed by protonation to generate intermediate **IV**. Intermediate **IV** eliminates a molecule of H_2O to produce the oxidation product **V**. Due to the fact that the covalent C–N bond showed a strongly oxidizing ability, a subsequent reduction of intermediate **V** by a lower valent Cu species followed by protonation releases the final product **2a** and ethyl acetate which was detected by MS analysis.

LC-MS analysis can provide important information about the intermediates of the reaction. To our delight, a clear spectrum was obtained when the reaction mixture was investigated by LC-MS. The 1-(2-ethoxy-2-oxoethyl)-4-alkylpyridin-1-ium chloride (**I**), which is formed by interaction between the 4-alkylpyridine and ethyl chloroacetate, was detected at *m*/*z* values of 194. Furthermore, the ketone coordinated to ethyl chloroacetate (**V**) was detected at *m*/*z* values of 208 by LC-MS analysis of the reaction mixture (for more details, see SI). These results proved that intermediate **I** and **V** participate in the catalytic cycle.

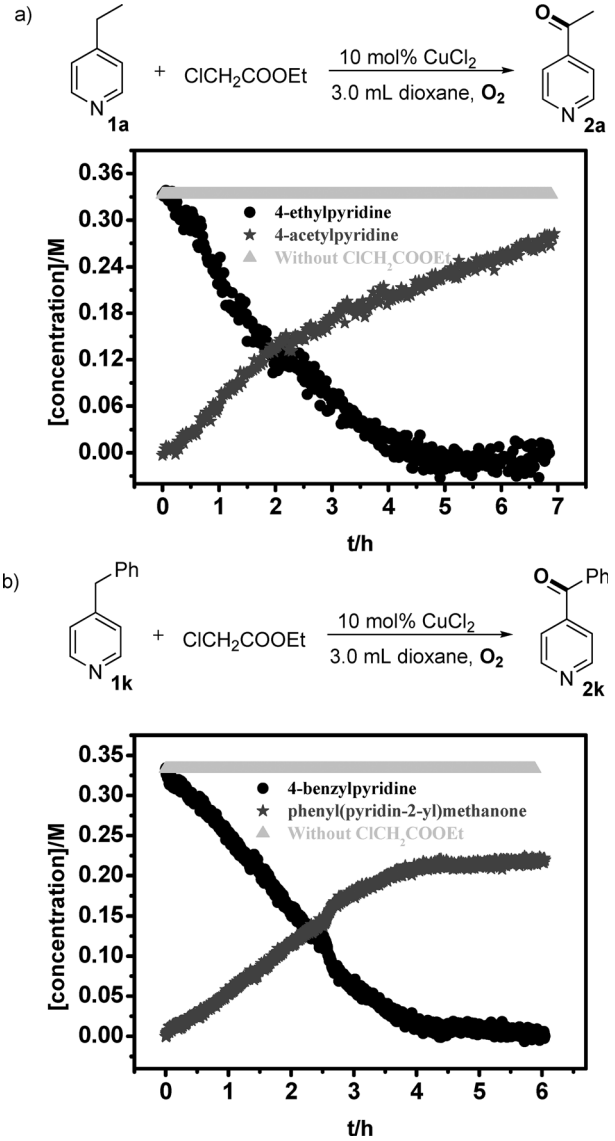


Figure 1. The 2D kinetic profiles of the oxidation of heterobenzylic methylenes. Reaction conditions: a) 4-ethylpyridine (1.0 mmol), ethyl chloroacetate (1.0 mmol), and $CuCl_2 \cdot 2H_2O$ (0.10 mmol) successively added to 1,4-dioxane (3.0 mL) at 100 °C. b) 4-Benzylpyridine (1.0 mmol), ethyl chloroacetate (1.0 mmol), and $CuCl_2 \cdot 2H_2O$ (0.10 mmol) successfully added to 1,4-dioxane (3.0 mL) at 100 °C.

The reactions were also monitored by in situ IR spectroscopy in the absence of ethyl chloroacetate (Figure 1). The kinetic profile clearly shows that 4-acetylpyridine and phenyl(pyridin-4-yl)methanone could not be observed without ethyl chloroacetate. Additionally, the two peaks of the product at 1713 cm^{-1} and 1675 cm^{-1} were observed. These results indicate that 4-substituted pyridines were successfully oxidized to the corresponding ketones under the standard reaction conditions promoted by ethyl chloroacetate, and that these reactions occurred without any inductive period as can be seen from the results of operando IR.

To confirm that an organic radical species is involved in the overall process, electron paramagnetic resonance (EPR) experiments were conducted to gain insight into the catalytic cycle. When ethyl chloroacetate in DMF and 4-ethylpyridine in DMF were tested, no signals were observed (Figure 2a,b).

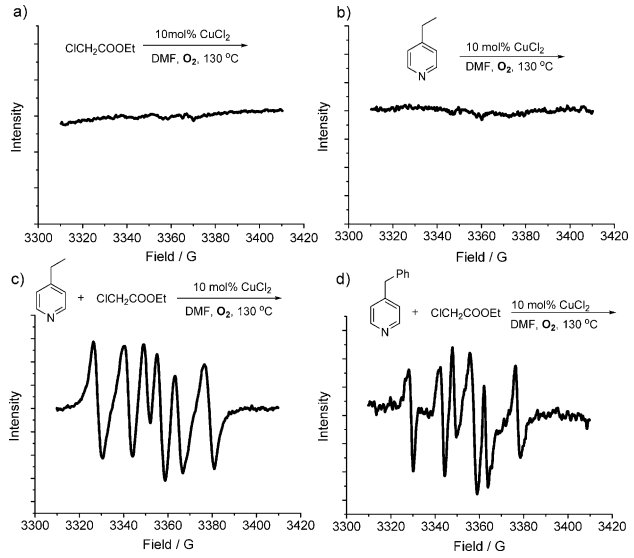


Figure 2. Eelectron paramagnetic resonance (EPR) spectra (X band, 9.4 GHz, room temperature).

However, the EPR spectrum of a mixture of 4-ethylpyridine, copper catalyst, and ethyl chloroacetate displayed a resonance characteristic of an organic radical with an absorption maximum at $g = 2.0030$ (Figure 2c). The organic radical could also be observed in the EPR spectrum of the mixture of 4-benzylpyridine, copper catalyst, and ethyl chloroacetate (Figure 2d). These EPR results confirmed the participation of organic radicals in the reaction system.

In conclusion, it was demonstrated that ethyl chloroacetate promoted the selective oxidation and functionalization of C_{sp^3}–H bonds to prepare the corresponding ketones with a copper catalyst and molecular oxygen. Interaction between the N-heterocyclic compounds and ethyl chloroacetate could activate the C–H bonds in the methylene group to easily prepare the ketones. The study of the substrate scope showed that various N-heterocyclic compounds were converted into the corresponding ketones with high selectivity and good to excellent yields by using molecular oxygen as the oxidant. Importantly, the effect of ethyl chloroacetate could provide valuable information for the further design of additives for selective copper-catalyzed direct oxidation and functionalization reactions of C_{sp^3}–H bonds.

Experimental Section

General procedure: $CuCl_2 \cdot 2H_2O$ (17 mg, 0.10 mmol) was added to an oven-dried Schlenk tube, which was sealed with a septum and fitted with an oxygen balloon. Subsequently, ethyl chloroacetate (1.0 mmol), 4-ethylpyridine (1.0 mmol), and DMF (3.0 mL) were injected using a syringe or microsyringe. Finally, the Schlenk tube was allowed to stir at 130 °C for 24 h. After completion, the reaction was quenched with water and the mixture was extracted with ethyl acetate (4 × 40 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel. The desired product was isolated as a colorless oil in 65 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.79$ (d, $J = 4.0$, 2H), 7.70 (dd, $J = 4.0$, 8.0 Hz, 2H), 2.61 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 197.3$, 150.9, 142.6, 121.2, 26.6 ppm. ESI-MS: 121(M)

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