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Copper-Catalyzed Aerobic Oxidative C−C Bond Cleavage of Unstrained Ketones with Air and Amines

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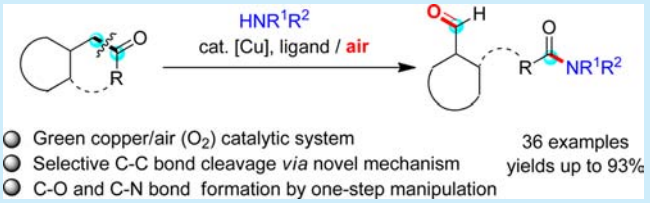
Supporting Information

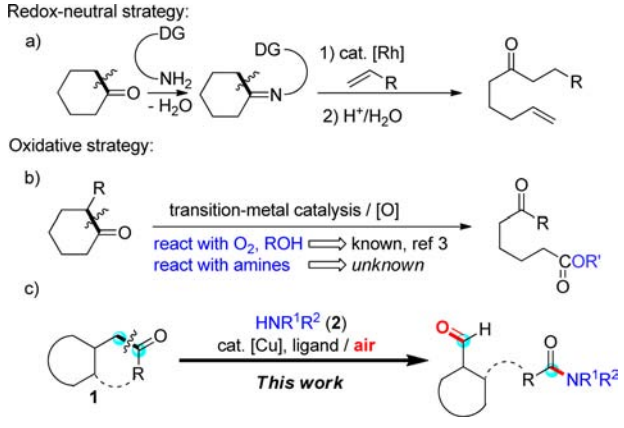
ABSTRACT: A unique copper-catalyzed aerobic oxidative C−C bond cleavage of simple unstrained ketones with air and amines has been developed. In this chemistry, amides and oxo amides are easily synthesized through the selective C−C bond cleavage of simple ketones or unstrained cycloketones. The broad substrate scopes and use of an inexpensive copper catalyst and green molecular oxygen as an oxidant as well as an O-source make this protocol very attractive for potential synthetic applications. The control experiments reveal that the present copper-catalyzed oxidative C−C bond cleavage of simple ketones proceeds in a novel catalytic pathway rather than through the cleavage of a dioxetane intermediate.



Transition-metal-catalyzed unstrained C−C bond cleavage enables a straightforward reconstruction strategy of carbon skeletons that could hardly be achieved by other means.[1−3] Among them, the ring opening reaction of simple substrates through C−C bond cleavage offers significant protocols for the construction of compounds containing two different functional groups. However, despite the significant ring-opening reactions of three- or four-membered rings, especially the strained cyclic ketones,[4,5] the selective C−C bond cleavage of an unstrained six- or seven-membered ring is still limited.

By using redox-neutral Rh-catalysis, Jun and co-workers pioneeringly disclosed a directing group assisted C−C bond activation process of unstrained cycloalkanone-imines and their skeletal rearrangement (Scheme 1a).[6] Alternatively, from simple ketones without a directing group, the transition-metal-catalyzed oxidative synthesis of oxo carboxylic acids has been significantly developed (Scheme 1b).[3] Recently, some advances on Cu-catalyzed aerobic oxidative C−C bond cleavage of simple ketones have been achieved.[7,8] Bi and Liu et al. reported a chemoselective oxidative C(CO)−C(methyl) bond cleavage of methyl ketones to aldehydes.[7] We disclosed the Cu-catalyzed highly selective C(CO)−C(alkyl) bond cleavage strategies for the construction of esters with alcohols,[8a] α-ketoesters with alcohols,[8b] primary amides with azide as a N-source,[8c] and acridones through an intramolecular C−H cyclization process.[8d] However, the direct transformation of simple ketones to amides using amines as a N-source has not been reported to date,[9] because (1) electron-rich primary and secondary amines are not stable under oxidative conditions[10] and (2) amines are very good ligands for binding the transition metal catalysts and inhibiting catalysis.[11] Therefore, the C−C bond cleavage of unstrained ketones with amines still offers a great challenge. Herein, we disclose for the first time a unique copper-catalyzed oxidative C−C bond cleavage of simple unstrained ketones and amines through an oxygenation process with air (Scheme 1c).

Scheme 1. Novel Route to Synthesize Amide from Ketone 1



Our studies initiated with the reaction of β-tetralone **1a** with aniline **2a**. A series of catalysts, ligands, and solvents were screened (Supporting Information (SI), Tables S1−S3). Under the optimized conditions [$CuCl_2 \cdot 2H_2O$ (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), mixed solvents ($V_{acetonitrile}/V_{1,4\text{-dioxane}}$ = 3/1, 2.0 mL), 40 °C, 24 h, air (1 atm)], the ring-opening product, 3-(2-formylphenyl)-*N*-phenyl propanamide **3aa**, was obtained in 71% isolated yield (Scheme 2). Further exploration indicates that both aryl and aliphatic

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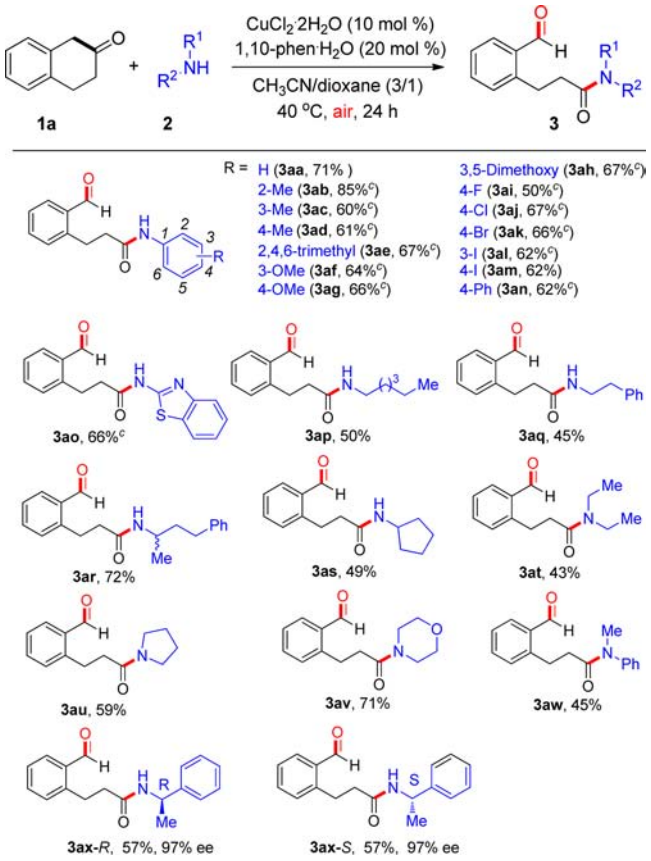
Scheme 2. Substrate Scope of Amines[a,b]



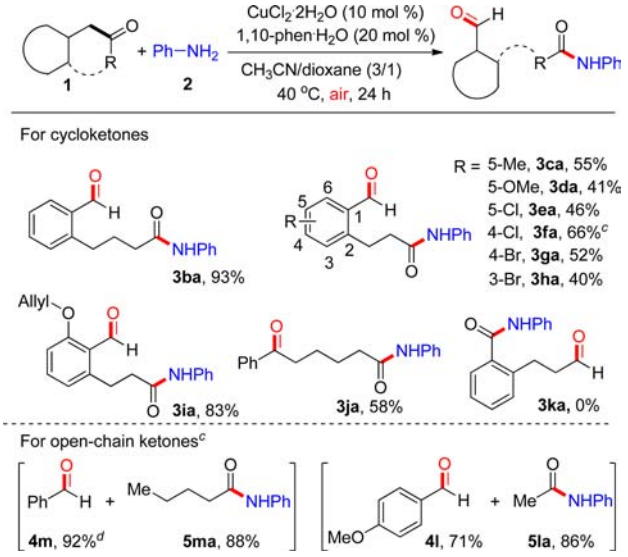
[a]Reaction conditions: a mixture of **1a** (0.50 mmol), **2** (0.25 mmol), $CuCl_2·2H_2O$ (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), and mixed solvents ($V_{acetonitrile}/V_{1,4\text{-dioxane}}$ = 3/1, 2.0 mL) was stirred at 40 °C for 24 h under air (1 atm). [b]Isolated yields. [c]Reflux.

primary amines performed well under the standard conditions, giving the desired oxo amides in moderate yields (**3ab**−**3as**). The scope of amines could be expanded to secondary amines (**3at**−**3aw**), showing that the compatibility of this transformation is remarkable. Furthermore, this transformation provided products without any deterioration in the enantiopurity originated from the starting amines, which makes it valuable in asymmetric synthesis (**3ax**-*R* and **3ax**-*S*).

Encouraged by these preliminary results, the scope of ketones was explored subsequently (Scheme 3). Under the standard conditions, seven-membered cycloketone could be successfully transformed into the product **3ba** in 93% yield. The reaction also showed a good tolerance for β-tetralones with varying functional groups (**3ca**−**3ia**). Notably, α-aryl cyclohexanone could be employed to furnish oxo amide **3ja** smoothly. However, no product was detected when α-tetralone was used (**3ka**). In addition, open-chain ketones were also selectively cleaved, giving the corresponding aldehydes and amides in good yields.

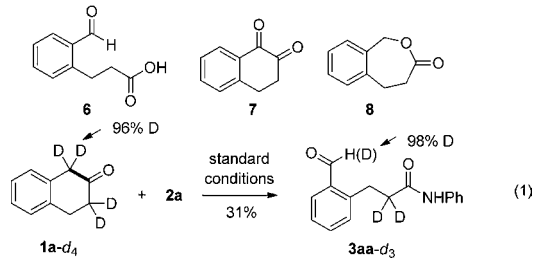
During the screening of reaction conditions, some oxo carboxylic acid **6**[12] and trace amounts of diketone **7** were detected in the reaction mixture. However, compounds **6** and **7** could not be converted into **3aa** under the standard conditions, indicating that they are not the intermediates for the formation of oxo amides (SI, eqs S1 and S2). Moreover, benzolactone **8** could not be transformed into **3aa**, suggesting that copper-catalyzed Baeyer−Villiger reaction may be not involved in this

Scheme 3. Substrate Scope of Ketones[a,b]



[a]Reaction conditions: a mixture of **1** (0.50 mmol), **2a** (0.25 mmol), $CuCl_2·2H_2O$ (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), and mixed solvents ($V_{acetonitrile}/V_{1,4\text{-dioxane}}$ = 3/1, 2.0 mL) was stirred at 40 °C for 24 h under air (1 atm). [b]Isolated yields. [c]Reflux. [d]GC yield.

transformation (SI, eq S3).[13] Interestingly, the reaction of β-tetralone-1,1,3,3-d_4 (**1a**-d_4) with **2a** affords **3aa**-d_3 with 98% deuterium incorporation in the aldehyde group (eq 1),



indicating that the reversible imine−enamine intermediates were not generated during the transformation, although the condensation of ketones and amines is very common. Therefore, the copper-catalyzed oxidative cleavage of enamine via a dioxetane intermediate[8a,14] is an unfavorable pathway (SI, Scheme S1).

To pursue the reaction mechanism in more detail, ^{18}O labeling experiments were conducted using ketone **1l** and aniline **2a** as substrates. The data listed in Table 1 suggest that (a) carbonyl oxygen on 4-methoxybenzaldehyde **4l** originates from O_2, which can readily exchange with water; (b) carbonyl oxygen on acetanilide **5la** comes mainly from ketone carbonyl oxygen and partially from water through oxygen exchange before the reaction; and (c) dioxetane may be not the intermediate of this reaction (SI, Scheme S1).

In addition, a set of experimental results imply that this reaction probably proceeds via a radical pathway (SI, Table S4). Interestingly, a 58% yield of oxo ester **9** and a trace amount of **3aa** were obtained by stoichiometric addition of TEMPO (Table 2, entry 1). It is noteworthy that aniline **2a** was indispensable for the formation of oxo ester **9** (entry 2). A 10 mol % loading of aniline could facilitate its formation up to 74% yield (entry 3). Moreover, oxo amide **3aa** could not be

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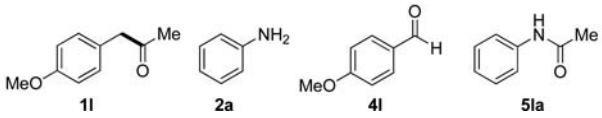
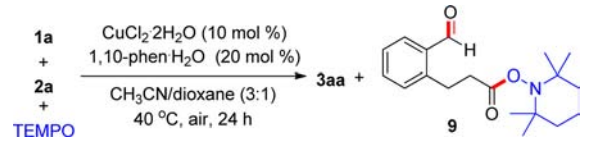
Table 1. ^{18}O Labeling Experiments[a]

entry	substrates (mmol)	^{18}O-reagent	products[b]
1[c]	**1l** (0.5) and **2a** (0.25)	$^{18}O2$	**4l**, 85%, $^{16}O/^{18}O$ = 0.8:1 **5la**, 65%, $^{16}O/^{18}O$ = 3.6:1
2[d]	**1l** (0.5) and **2a** (0.25)	$H_2{}^{18}O$	**4l**, 77%, $^{16}O/^{18}O$ = 1.2:1 **5la**, 71%, $^{16}O/^{18}O$ = 4.7:1
3[d]	**1l** (0.5)	$H_2{}^{18}O$	**1l**, $^{16}O/^{18}O$ = 1.16:1
4[d]	**4l** (0.25)	$H_2{}^{18}O$	**4l**, $^{16}O/^{18}O$ = 2.07:1
5[d]	**5la** (0.25)	$H_2{}^{18}O$	**5la**, $^{16}O/^{18}O$ = 100:0



[a]Reaction conditions: a mixture of substrates, $CuCl_2$ (10 mol %), 1,10-phen (20 mol %), and anhydrous mixed solvents ($V_{acetonitrile}/V_{1,4\text{-dioxane}}$ = 3/1, 2.0 mL) was stirred under O_2 (1 atm) reflux for 24 h. [b]Isolated yields. The ratio of ^{16}O to ^{18}O on products was determined by GC-MS. [c]The reaction was carried out under $^{18}O_2$ (1 atm) instead of O_2. [d]The reaction was carried in the presence of $H_2{}^{18}O$ (5 equiv).

Table 2. Formation of Oxo Ester 9[a]



entry	substrates (mmol)	yield (%) 3aa	9
1	**1a** (0.5), **2a** (0.25), TEMPO (0.25)	trace	58
2	**1a** (0.5), **2a** (0), TEMPO (0.25)	0	trace
3	**1a** (0.5), **2a** (10 mol %), TEMPO (0.25)	0	74

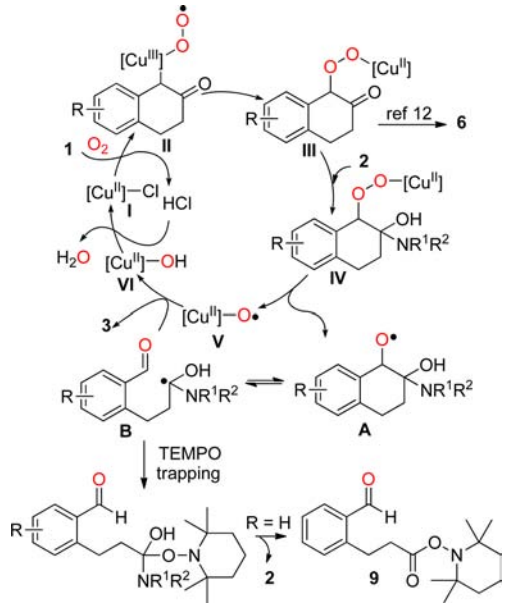
[a]Isolated yields based on 0.25 mmol scale. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

converted into oxo ester **9** in the presence of TEMPO under standard conditions (SI, eq S4).

On the basis of the above investigations and the reported literature, a plausible mechanism is proposed (Scheme 4). The catalytic cycle starts with the reaction of copper complex **I** with ketone **1** and dioxygen[15] to give peroxycopper(III) species **II**. Subsequent isomerization affords peroxide **III**,[16] which also leads to the formation of oxo acid simultaneously.[12] Intermediate **IV** formed through the nucleophilic attack of amine **2** to species **III** undergoes homolytic cleavage of O−O bond, giving copper species **V**[17] and intermediate **A**. Radical species **B**,[18] resulting from β-fragmentation of radical **A** in a reversible way,[19] could be further in turn oxidized by species **V** to furnish the desired product **3** and liberate [Cu(II)−OH] species **VI**, which delivers the catalyst with the aid of hydrochloride to initiate a new catalytic cycle. Radical species **B** can be trapped by TEMPO,[20] followed by the release of amine **2** to provide oxo ester, which is consistent with the result carried out under a catalytic loading of aniline **2a** (Table 2, entry 3). This also can reasonably explain the result obtained in the labeling experiments (Table 1).

In summary, we have developed a copper/air catalytic system for aerobic oxidative C−C bond cleavage of unstrained ketones

Scheme 4. Proposed Mechanistic Pathway



with amines. In this chemistry, primary and secondary amines were employed for the selective C−C bond cleavage of simple ketones or unstrained cycloketones. The broad substrate scopes and use of an inexpensive copper catalyst and green molecular oxygen as an oxidant as well as O-source make this protocol very attractive for potential synthetic applications. The control experiments reveal that the present copper-catalyzed oxidative cleavage of simple ketones proceeds in a novel catalytic pathway rather than through the cleavage of a dioxetane intermediate. A novel catalytic cycle is proposed based on the preliminary mechanism studies. Further studies on the synthetic applications of this method are ongoing in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, analytical data for products, NMR spectra of products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01114.

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Notes

The authors declare no competing financial interest.

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