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Oxygen-Involved Oxidative Deacetylation of α-Substituted β-Acetyl Amides – Synthesis of α-Keto Amides

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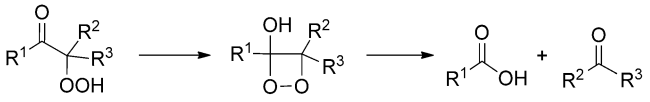
Abstract: α-Substituted β-acetyl amides could undergo C–C bond cleavage to form α-keto amides when treated with copper(II) chloride ($CuCl_2$) and boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) under an oxygen atmosphere. The yield can be increased by the addition of *tert*-butyl hydroperoxide which alone can also effect the reaction. The reaction provides a new protocol for the synthesis of α-keto amides.

Keywords: β-acetyl amides; *tert*-butyl hydroperoxide; copper catalysis; α-keto amides; oxidative deacetylation; oxygen

The single electron oxidation of enolates by transition metals such as Mn^{3+}, Ce^{4+}, Cu^{2+}, Co^{3+}, Fe^{3+} and Ag^{+} etc. would generate α-carbonyl radicals, and this transformation forms the basis of a variety of synthetically useful intramolecular and intermolecular oxidative C–C bond forming methods.[1] When the reactions are carried out in the presence of oxygen, the α-carbonyl radicals would be captured by oxygen to form peroxy radicals and then α-peroxy ketones or aldehydes,[2] which would subsequently transform to 1,2-dioxetane intermediates and then undergo C–C bond cleavage to yield two carbonyl fragments (Scheme 1).[3,4,5] This process has found synthetic applications by using cerium(IV) ammonium nitrate[4] or copper salts[5] as oxidant.



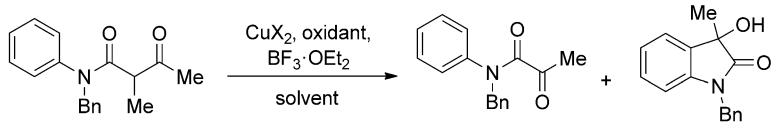
Scheme 1.

Recently, Kündig et al.[6] and Taylor et al.[7] independently reported the synthesis of 3,3′-disubstituted oxindoles from *N*-phenyl amides. This methodology involves the oxidation of the *N*-phenyl amide-derived enolate by copper salts to the corresponding carbon radical, which then undergoes intramolecular attack to the phenyl ring. Later on, Taylor et al. improved the method by using copper as catalyst and oxygen as oxidant.[8] These conditions work very well for α-substituted *N*-phenyl β-alkoxycarbonyl (or aminocarbonyl) amides. Besides its synthetic usefulness, it should be pointed out that under an oxygen atmosphere, the capture of α-alkyloxycarbonyl radicals or α-aminocarbonyl radicals by oxygen is not fast enough to compete with the intramolecular cyclization. In continuation of our interest in the free radical reactions of β-carbonyl amides,[9] we recently found that when α-substituted *N*-phenyl β-acetyl amides (**1**) were treated with $CuCl_2$ and $BF_3{\cdot}OEt_2$ under aerobic conditions, the oxidative deacetylation products α-keto amides (**2**) were generated. The formation of **2** involves the trapping of α-carbonyl radicals by molecular oxygen as the key step. The yield of **2** can be improved by the addition of *tert*-butyl hydroperoxide (TBHP, 70% in water). Herein we wish to report the detailed results.

Our study was initiated by subjecting compound **1a** to some common copper salts in an oxygen atmosphere under a variety of conditions. The results are summarized in Table 1.

It can be seen from Table 1 that when treated with 0.1 equiv. of $CuCl_2$ and 2.0 equiv. of $BF_3{\cdot}OEt_2$ in CH_3CN, **1a** was converted to α-keto amide **2a** in moderate yield (entries 3 and 5, Table 1). The reaction did not take place without $BF_3{\cdot}OEt_2$ (entry 1, Table 1). Compound **2a** was also generated with $CuBr_2$, $Cu(OAc)_2$ or $Cu(OTf)_2$, but the yield was lower. Besides **2a**, a small amount of cyclization product **3a** was obtained in varying yields in most cases; **3a** is apparently derived from the acid-catalyzed intramolecular Friedel–Crafts reaction of **2a**.[10] Among the solvents

Table 1. The reaction of **1a** with oxygen under various conditions.

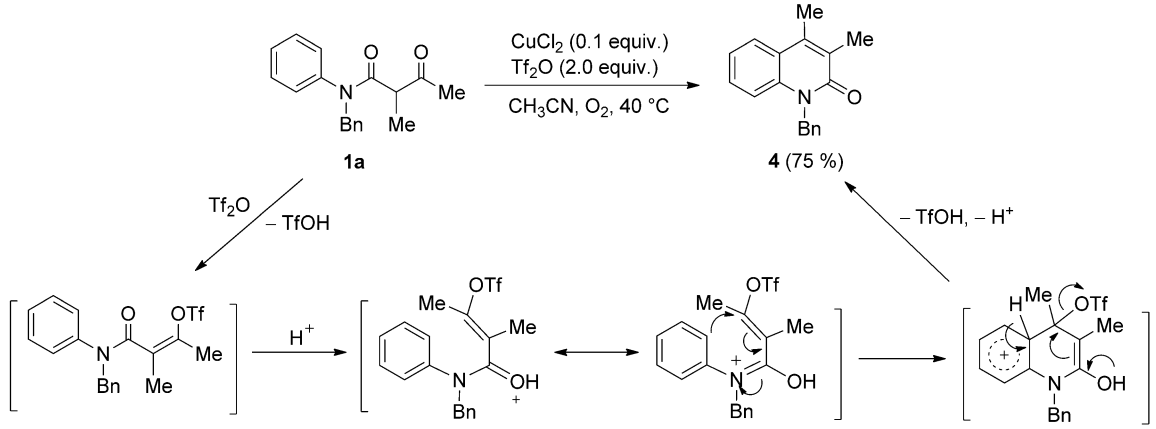


1a **2a** **3a**

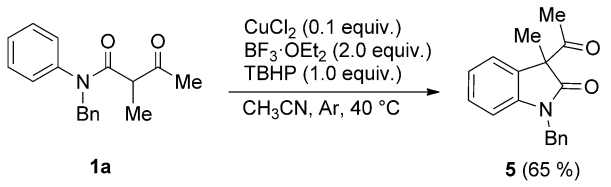
Entry	CuX_2 (equiv.)	Oxidant	Equiv. of BF_3·OEt	Solvent (Temp.)	Reaction time [h]	Products (yield [%])[a]
1	$CuCl_2$ (0.1)	O_2	none	CH_3CN (r.t.)	24	N.R.
2	$CuCl_2$ (0.1)	O_2	1.0	CH_3CN (r.t.)	30	**2a** (15), **3a** (3)
3	$CuCl_2$ (0.1)	O_2	2.0	CH_3CN (r.t.)	20	**2a** (40), **3a** (5)
4	$CuCl_2$ (1.0)	O_2	2.0	CH_3CN (40 °C)	15	**2a** (25), **3a** (6)
5	$CuCl_2$ (0.1)	O_2	2.0	CH_3CN (40 °C)	8	**2a** (45), **3a** (5)
6	none	O_2	2.0	CH_3CN (40 °C)	20	**2a** (10), **3a** (trace)
7	$CuCl_2$ (0.1)	O_2	3.0	CH_3CN (40 °C)	8	**2a** (40), **3a** (6)
8	$CuCl_2$ (0.1)	O_2	2.0	toluene (40 °C)	12	**2a** (5), **3a** (0)
9	$CuCl_2$ (0.1)	O_2	2.0	THF (40 °C)	12	**2a** (30), **3a** (3)
10	$CuCl_2$ (0.1)	O_2	2.0	CH_2Cl_2 (r. t.)	24	**2a** (0), **3a** (0)
11	$CuBr_2$ (0.1)	O_2	2.0	CH_3CN (40 °C)	10	**2a** (30), **3a** (10)
12	$CuOAc_2 \cdot 2H_2O$ (0.1)	O_2	2.0	CH_3CN (40 °C)	10	**2a** (10), **3a** (25)
13	$Cu(OTf)_2$ (0.1)	O_2	2.0	CH_3CN (40 °C)	12	**2a** (22), **3a** (10)
14	$CuSO_4 \cdot 5H_2O$ (0.1)	O_2	2.0	CH_3CN (40 °C)	12	N.R.
15	$Cu(NO_3)_2$ (0.1)	O_2	2.0	CH_3CN (40 °C)	12	N.R.
16	$CuCl_2$ (0.1)	O_2 + TBHP[b]	2.0	CH_3CN (r. t.)	4	**2a** (61), **3a** (trace)
17	$CuCl_2$ (0.1)	O_2 + TBHP[b]	2.0	CH_3CN (40 °C)	3	**2a** (70), **3a** (4)
18	**$CuCl_2$ (0.1)**	**O_2 + TBHP[c]**	**2.0**	**CH_3CN (40 °C)**	**3**	**2a (82),** **3a** (trace)
19	none	O_2 + TBHP[b]	2.0	CH_3CN (40 °C)	8	**2a** (42), **3a** (4)
20	none	O_2 + TBHP[c]	2.0	CH_3CN (40 °C)	8	**2a** (48), **3a** (6)
21	none	O_2 + TBHP[b]	none	CH_3CN (40 °C)	12	N.R.

[a] Isolated yields.
[b] 1.0 equiv. of TBHP was used.
[c] 2.0 equiv. of TBHP was used.

examined, CH_3CN proved to be the most suitable reaction medium. The appropriate reaction temperature was found to be from room temperature to 40 °C. At higher temperature decomposition became dominant. In order to raise the yield of **2a**, we tried using several other acids such as TMSOTf, $InCl_3$, $BiCl_3$, $Zn(OTf)_2$ and CF_3COOH in place of BF_3·OEt_2, but they were all less effective. It is interesting to see that when triflic anhydride was used, the reaction afforded **4** rather than **2a** and **3a** (Scheme 2), and the reaction proceeded as well in the absence of $CuCl_2$. This transformation is known to take place under strong acidic conditions.[11] The triflic anhydride-promoted process can be rationalized by the mechanism shown in Scheme 2.



Scheme 2.

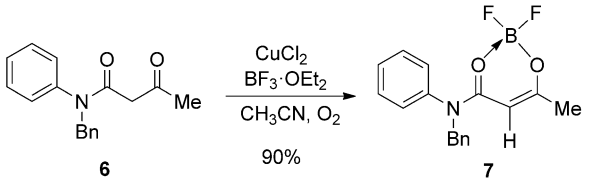


Scheme 3.

Finally, we found that adding TBHP (70% in water) to the reaction system could increase the yield of **2a** remarkably at 40 °C (entries 17 and 18, Table 1). Control experiment shows that TBHP alone in the absence of copper is capable of prompting the reaction, albeit with lower yield (entries 19 and 20, Table 1). But still $BF_3{\cdot}OEt_2$ is a necessary condition (entry 21, Table 1).

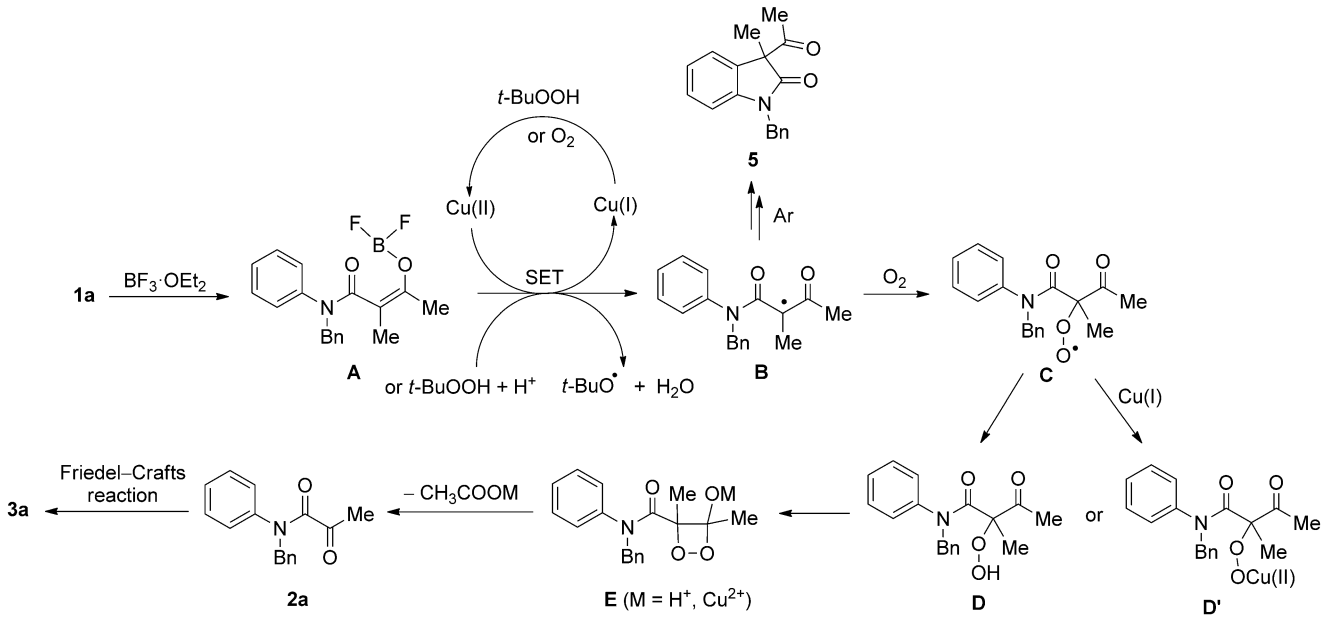
When the reaction was performed under an argon atmosphere under otherwise the same conditions, oxindole product **5** was obtained (Scheme 3). This reaction was formerly realized by using Ag_2O as the oxidant.[9a]

Nair et al. previously reported a relevant transformation of α-unsubstituted acetoacetamides to oxamates under an oxygen atmosphere by using 2 equiv. of cerium(IV) ammonium nitrate (CAN) as the single electron oxidant.[4b] However, it was found that the reaction did not take place when **1a** was treated with CAN under Nair's conditions. On the other hand, when our procedure was applied to compound **6**, the expected oxidative C–C bond cleavage did not take place. Instead, boron enolate **7** was obtained. The structure of **7** proved to be very stable[12] and it cannot be oxidized under the present conditions (Scheme 4).



Scheme 4.

The formation of compound **2a** can be rationalized with the free radical mechanism illustrated in Scheme 5: compound **1a** first tautomerizes to its enolate form **A**[13] by the action of $BF_3{\cdot}OEt_2$, and then is oxidized to α-carbonyl radical **B** *via* a single electron transfer process. Control experiment indicates that the tautomerization is a quite facile process. The direct α-hydrogen abstraction can be ruled out as no reaction took place in the absence of $BF_3{\cdot}OEt_2$. Both $CuCl_2$ and TBHP could act as oxidant. In addition, the reaction of $CuCl_2$ and TBHP might produce a more powerful oxidizing species, as the combination of $CuCl_2$ and TBHP led up to a much better yield. It might be Cu(II)OO-*t*-Bu, *t*-BuO•, or *t*-BuOO•, since all these species might be generated in the reaction system.[14] To evaluate the effect of *t*-BuO• on the reation, we did a control experiment by replacing $CuCl_2$ with CuBr. The *t*-BuO• radical is believed to be a major oxidizing species in the system of Cu(I) and *t*-BuOOH. We found that the yield of **2a** was only 44% when CuBr and *t*-BuOOH were used. This result suggests that *t*-BuO• may not be important in the present case. A reasonable hypothesis is that Cu(II)OO-*t*-Bu might be responsible for the enhanced performance



Scheme 5. Proposed mechanism for the formation of **2a**, **3a** and **5** from **1a**.

of the $CuCl_2$/*t*-BuOOH system. However, the participation of *t*-BuOO· cannot be ruled out despite the fact that it does not usually act as a single electron oxidant.

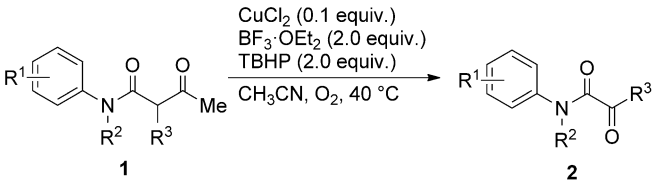
Following the SET step, radical **B** would be trapped by oxygen to generate peroxy radical **C**, and then peroxide **D** (**D′**), which is converted to **2a** in two steps. It is also possible that radical **C** might directly undergo cyclization to afford the 1,2-dioxetane intermediate.[15] In the absence of oxygen, **B** would undergo radical cyclization to give **5**. This result is different from that reported by Taylor et al.[8] in that in their cases, α-carbonyl radicals can be converted to oxindoles *via* intramolecular oxidative coupling in high yields under an oxygen atmosphere. Besides the structural features, the acidic conditions adopted in the present work might also have some influence on the reaction consequences.

α-Keto amide is an important structural moiety occurring in many bioactive natural products, and its construction has long been of interest to synthetic chemists.[16,17] Recently, Jiao et al.,[17a–c] Mai et al.,[17d] and Ji et al.[17e] reported several efficient syntheses of α-keto amides which employ the copper-catalyzed oxidative coupling reactions with molecular oxygen as oxidant. In another study, α-keto amides were prepared from the aerobic oxidation of arylacetamides.[18] These methods are suitable for the synthesis of aromatic α-keto amides, but have not been used to prepare their counterparts bearing alkyl groups at the α-position. We expected that the reaction described herein would constitute a complement to the above-mentioned oxidative methods. With this in mind, next we applied this protocol to a variety of *N*-aryl β-acetyl amides (**1b**–**1q**) to examine the scope of the reaction, and the results are listed in Table 2.

Under the optimized reaction conditions (entry 18, Table 1), compounds **1** were converted to the corresponding α-keto amides in varying yields except for **1n** (entry 14, Table 2), in which case the reaction only resulted in the formation of a complex mixture. The yields were also low for compounds **1l** and **1m** (entries 12 and 13, Table 2). Apart from these cases, α-keto amides **2** were obtained in good yields for other substrates.

In contrast to these results, the reaction of the *N*-monosubstituted compound **1r** afforded a mixture of α-keto amide (**2r**), α-*tert*-butylperoxy product (**8**) and α-hydroxylation product (**9**) under the same conditions. Compound **8** was found to transform *in situ* into **9** (Scheme 6). The different behavior of **1r** as compared with **1a**-**1q** might be explained by the lack of an alkyl group at the *N* atom in **1r**. It is reasonable to believe that compound **8** results from the oxidation of the **1r**-derived radical by Cu(II)OO-*t*-Bu.[14] This reaction is supposed to be unfavorable for substrates **1a**–**1q** due to the steric hindrance caused by the substituents at the nitrogen atom. However, in the case of **1r**, the steric hindrance gets relieved, and its trapping by Cu(II)OO-*t*-Bu is made possible. It should be noted that the formation of **8** is consistent with the presence of Cu(II)OO-*t*-Bu in the current reaction system.

Table 2. $CuCl_2$-catalyzed oxidative transformations from **1** to **2**.[a]

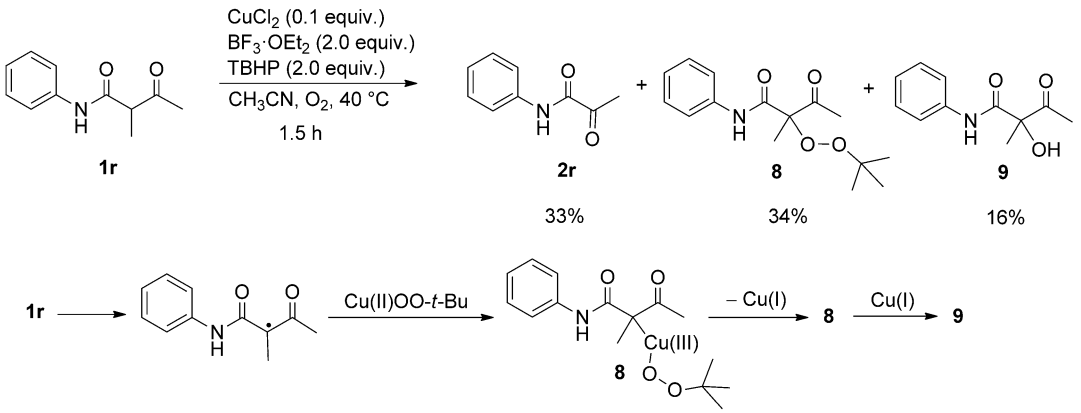


Entry	1	R^1	R^2	R^3	Product 2	Yield [%][b]
1	**1a**	H	Bn	Me	**2a**	82
2	**1b**	*p*-Me	Bn	Me	**2b**	78
3	**1c**	*p*-MeO	Bn	Me	**2c**	76
4	**1d**	*p*-Br	Bn	Me	**2d**	81
5	**1e**	*p*-Cl	Bn	Me	**2e**	66
6	**1f**	*p*-I	Bn	Me	**2f**	58
7	**1g**	*p*-F	Bn	Me	**2g**	77
8	**1h**	*m*-Me	Bn	Me	**2h**	83
9	**1i**	*m*-Br	Bn	Me	**2i**	89
10	**1j**	*o*-Me	Bn	Me	**2j**	61
11	**1k**	H	Bn	Et	**2k**	81
12	**1l**	H	Bn	Bn	**2l**	42
13	**1m**	H	Bn	4-MeBn	**2m**	44
14	**1n**	H	Bn	allyl	**2n**	–[c]
15	**1o**	H	Me	Me	**2o**	71
16	**1p**	H	Et	Me	**2p**	65
17	**1q**	H	Bn	*n*-Bu	**2q**	58

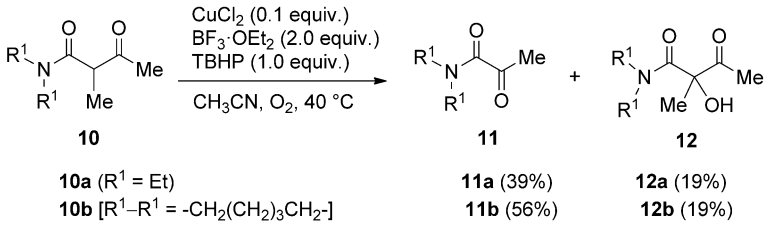
[a] The reaction was conducted on 0.5 mmol scale in 5 mL CH_3CN.
[b] Isolated yield.
[c] Complex mixture.

When compounds **10** were subjected to the conditions, mixed results were obtained (Scheme 7 and Scheme 8). In the case of **10a** and **10b**, the reaction produced **12** besides the desired α-keto amides **11** (Scheme 7), while α-keto amide products were obtained predominantly when the α-methyl group was replaced by Bn (Scheme 8). The formation of **12a** and **12b** might also be due to the lesser steric hindrance of the methyl group in **10a** and **10b**. For these substrates, using 1.0 equiv. or 2.0 equiv. of TBHP did not make apparent difference in the yields of the products.

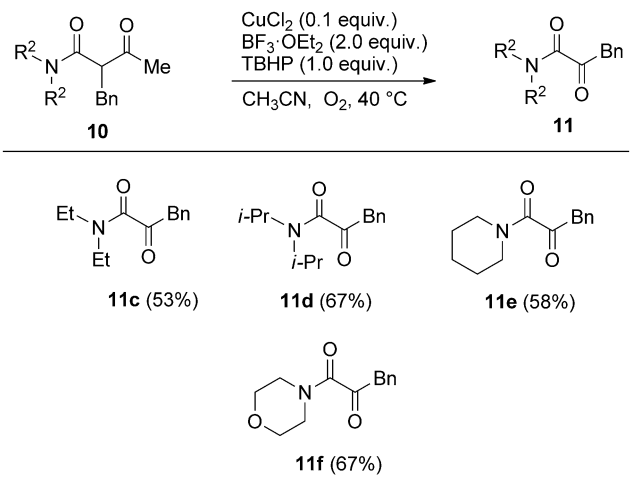
N-Aryl α-keto amides can react *via* the intramolecular Friedel–Crafts reaction to form 3-hydroxyindoles.[10] As aforementioned, we did find a small amount of 3-hydroxyindole products **3** along with **2** in the reaction mixture (Table 1). An attempt was then made to maximize the yields of **3**. After some explorations, we found that adding one more portion of $CuCl_2$ and $BF_3{\cdot}OEt_2$ to the reaction mixture after **1** was completely consumed and then allowing the re-



Scheme 6.



Scheme 7.



Scheme 8.

action to continue under an argon atmosphere at 60 °C gave **3** in moderate yields (Scheme 9).

In summary, we have demonstrated that the oxidizing system of $CuCl_2$/*t*-BuOOH/O_2 can affect the oxidation of α-substituted β-acetyl amides in the presence of $BF_3{\cdot}OEt_2$. The reaction results in the formation of oxidative deacetylation products α-keto amides in moderate to good yields. The procedure described herein provides an alternative protocol for the synthesis of aliphatic α-keto amides. Furthemore, on the basis of this process, a one-pot synthesis of 3-hydroxyindoles from α-substituted β-acetyl amides has been developed.

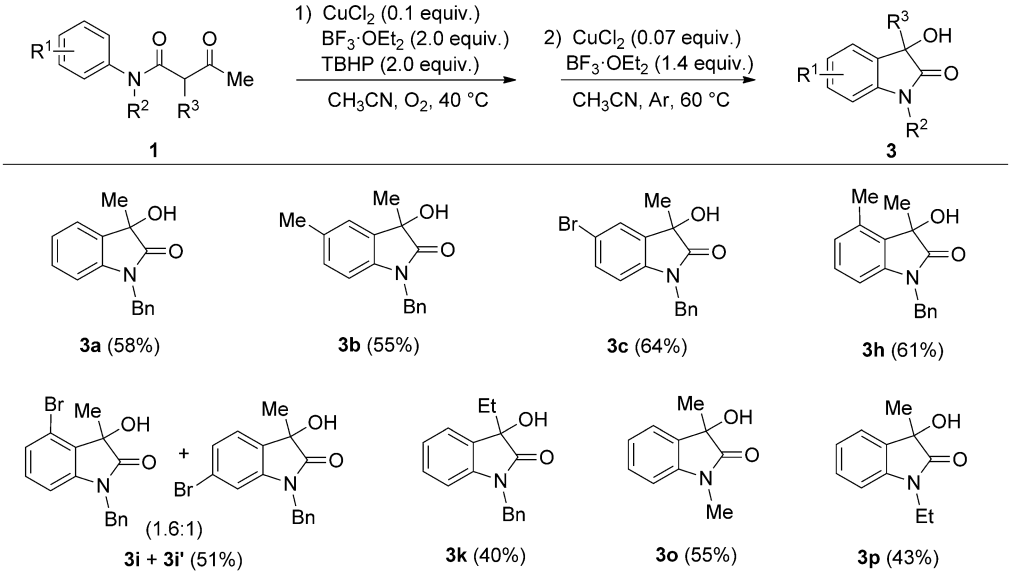
Experimental Section

General Methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$. The chemical shifts in ^{1}H NMR spectra were determined with $(CH_3)_4Si$ as the internal standard ($\delta = 0.00$ ppm). The chemical shifts in ^{13}C NMR spectra were determined based on that of $CDCl_3$ ($\delta = 77.00$ ppm). The EI-mass spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HR-MS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI or a Bruker micrOTOF QII by ESI. Melting points were measured on an XT-4 melting point apparatus and are uncorrected. Flash column chromatography was carried out with silica gel (200–300 mesh). α-Substituted β-acetyl amides were prepared according to the previous literatures.[7,19]

General Procedure for the Reactions of α-Substituted β-Acetyl Amides (1)

To a 25-mL round-bottom flask equipped with a magnetic stirring bar were added **1** (0.5 mmol), anhydrous $CuCl_2$ (6.8 mg, 0.05 mmol), $BF_3{\cdot}OEt_2$ (125 μL, 1.0 mmol), *tert*-butyl hydroperoxide (TBHP, 70% in water) (140 μL, 1.0 mmol) and CH_3CN (5 mL). The mixture was stirred in an oil bath at 40 °C. After the reaction complete as indicated by TLC



Scheme 9.

(generally 2–3 h), the reaction mixture was poured into saturated aqueous NH_4Cl solution (15 mL), and was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (30 mL) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was treated with silica gel chromatography to give products **2**.

General Procedure for the Preparation of 3-Hydroxyindoles (3)

To a 25-mL round-bottom flask equipped with a magnetic stirring bar was added **1** (0.5 mmol), anhydrous $CuCl_2$ (6.8 mg, 0.05 mmol), $BF_3{\cdot}OEt_2$ (125 μL, 1.0 mmol), *tert*-butyl hydroperoxide (TBHP, 70% in water) (140 μL, 1.0 mmol) and CH_3CN (5 mL). The solution was stirred in an oil bath at 40 °C. After the substrate was consumed as indicated by TLC, another portion of anhydrous $CuCl_2$ (5 mg) and $BF_3{\cdot}OEt_2$ (88 μL) was added to the reaction mixture, and the stirring was continued at 60 °C under an argon atmosphere. After completion of reaction, the reaction mixture was poured in saturated aqueous NH_4Cl solution (15 mL), and the mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (30 mL) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was treated with silica gel chromatography to give **3**.

Acknowledgements

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