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Copper-Catalyzed Annulation of Oxime Acetates with α-Amino Acid Ester Derivatives: Synthesis of 3-Sulfonamido/Imino 4-Pyrrolin-2-ones

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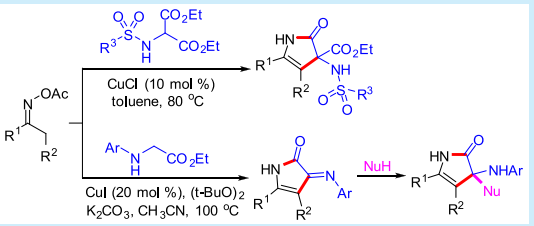
ABSTRACT: A copper-catalyzed annulation of oxime acetates and α-amino acid ester derivatives for the easy preparation of 4-pyrrolin-2-ones bearing a 3-amino group has been developed. This process features the oxidation of amines with oxime esters as the internal oxidant to produce the active 1,3-dinucleophilic and 1,2-dielectrophilic species concurrently. The subsequent nucleophilic cyclization realizes the efficient construction of 4-pyrrolin-2-one derivatives.



The efficient construction of functional heterocycles in a simple way is an important task in synthetic chemistry. Among the widely existing five-membered nitrogen-containing heterocycles, the 4-pyrrolin-2-one core represents an important motif, which has been found in many natural products such as cyanogramide[1] and violacein[2] (Figure 1) and reported to exhibit various biological activities including reducing cholesterol uptake,[3] antitumoral,[4] antibiotic,[5] and analgesic properties,[6] etc. Diketopyrrole, which has two fused 4-pyrrolin-2-one skeletons, has been used as a versatile building block in organic solar cells as an electron acceptor[7] as well as a fluorescent probe for the detection of biologically important species.[8] Therefore, the exploitation of new methods for construction of such scaffolds with structural diversity is of high interest, which can be seen from the recent numerous works, such as copper-mediated reaction of enamines with α-bromocarbonyls or *N*-(2-pyridylcarbonyl) amino acid ester,[9] $K_2S_2O_8$/TEMPO-induced oxidative cyclization of *N*-unprotected enaminocarbonyls,[10] Eosin Y/$Cu(OAc)_2$ or $Mn(OAc)_2$-catalyzed annulation of vinyl azides with ketene silyl acetals or 4-hydroxycoumarins,[11] Cu-catalyzed aminodifluoroalkylation of alkynes and bromodifluoroacetamides,[12] Rh-catalyzed diazooxindoles with vinyl isocyanates or *N*-pivaloyloxy acrylamides,[13] oxidative dearomatization of pyrroles,[14] copper-catalyzed tandem reaction of vinylalkynes, imines, and α,β-unsaturated acid chlorides,[15] and photooxidation of 2-substituted furans.[16] However, some drawbacks still existed, such as not easily available raw materials, substrate limit, and the use of expensive catalyst.

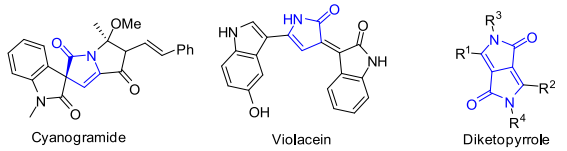


Figure 1. Biologically active and functional molecules containing a 4-pyrrolin-2-one moiety.

Oxime esters, which can be easily prepared from carbonyl compounds, have a very high reactivity due to the existence of an easily broken N−O bond. In the past several years, oxime esters have emerged as a versatile platform for the synthesis of diverse nitrogen-containing heterocycles via [3+*n*]-type reaction.[17] Therein, various five-membered heterocycles including pyrroles,[18] pyrrolines,[19] oxazoles,[20] thiazoles,[21] imidazoles,[22] pyrazoles,[23] triazoles[24] (Scheme 1a), and six-membered heterocycles such as pyridines[25] were constructed efficiently. Exploring their application in the synthesis of new heterocyclic scaffolds is challenging and interesting. Most recently, we developed a $Cu(OAc)_2$-promoted reaction of malonate-tethered oxime ester with indole derivatives for the synthesis of polysubstituted 3-pyrrolin-2-ones.[26] In continuing our efforts aimed at extending the application of oxime esters for constructing new nitrogen-containing frameworks, herein, we reported a redox strategy to synthesize 4-pyrrolin-2-ones from oxime esters and α-amino acid ester derivatives.

Amines were very easily oxidized to form imines or imine cations *in situ*, which reacted with nucleophiles to afford a series of α-functionalized amines.[27] It has been reported that amines acted as electrophilic carbon synthons in their reactions with oxime esters catalyzed by [Ru], [Fe], or I_2 to form

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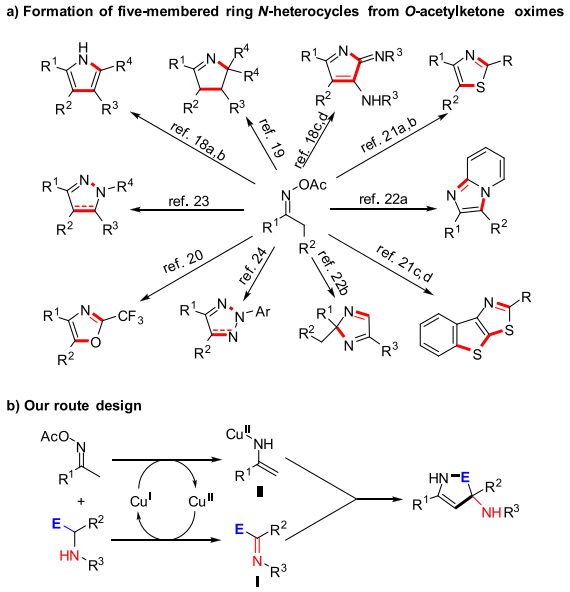
Scheme 1. Construction of Five-Membered Nitrogen-Containing Heterocycles Based on the Oxime Esters

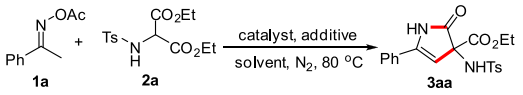


pyridines accompanied by the C−N bond cleavage.[28] Herein, we introduced an electrophilic center on the α-carbon of secondary amines and envisaged using oxime esters as an internal oxidant to oxidize the amines to imine intermediates **I** having two vicinal electrophilic centers. Meanwhile, an active 1,3-dinucleophilic enamino-Cu^{II} species **II** was generated simultaneously. The further interaction would lead to structurally diverse five-membered 3-amino nitrogen-contaning heterocycles (Scheme 1b).

To validate this idea, our initial studies were carried out using oxime acetate **1a** and diethyl 2-((4-methylphenyl) sulfonamido) malonate **2a** as the substrates (Table 1). When CH_3CN was used as the solvent, only a trace of the desired product **3aa** was formed in the presence of CuCl (0.1 equiv) under a N_2 atmosphere at 80 °C (entry 1). A solvent survey showed that toluene was the best solvent to realize the cyclization to give **3aa** in 80% yield within 4 h (entries 2−5). Other copper salts including CuI, CuBr, $Cu(OAc)_2$, $CuCl_2$, CuCN, CuSCN, and $Cu(OTf)_2$ were also screened, and CuCl was still the most effective (entries 5−12). $Pd(PPh_3)_4$ and $FeCl_2$, which were commonly used in the transformation of oxime esters, did not exhibit catalytic activity (entries 13 and 14). The addition of K_2CO_3 blocked the reaction severely (entry 15). An organic base such as DMAP and DABCO as additives has no significant influence on the yield (entries 16 and 17). In the absence of CuCl, no **3aa** was generated (entry 18). Further decreasing the amount of CuCl to 5 mol % led to a lower yield with a longer reaction time (entry 19).

With the optimized cyclization procedure established, the generality of the CuCl-catalyzed annulation was examined (Scheme 2). The scope of the oxime esters was first explored with **2a** as the coupling partner. Various aryl ethyl ketoxime acetates bearing either an electron-donating or electron-withdrawing group on the phenyl ring were broadly tolerated, giving the annulation products **3aa**−**3ja** in moderate to good yield (51−80%). Heterocyclic oxime acetates linking a pyridyl, pyrazinyl, furyl, and thienyl group on the oxime acetates were also compatible with this process, providing the corresponding products **3ka**−**3na** in 54−70% yields. Changing the R^2 group

Table 1. Screening of the Reaction Conditions[a]



entry	catalyst	solvent[b]	additive	yield (%)[b]
1	CuCl	CH_3CN	-	trace
2	CuCl	1,4-dioxane	-	60
3	CuCl	$CH_3CO_2Bu^n$	-	69
4	CuCl	DCE	-	73
5	CuCl	toluene	-	80
6	CuI	toluene	-	67
7	CuBr	toluene	-	16
8	$Cu(OAc)_2$	toluene	-	12
9	$CuCl_2$	toluene	-	48
10	CuCN	toluene	-	trace
11	CuSCN	toluene	-	trace
12	$Cu(OTf)_2$	toluene	-	trace
13	$Pd(PPh_3)_4$	toluene	-	trace
14	$FeCl_2$	toluene	-	trace
15	CuCl	toluene	K_2CO_3	9
16	CuCl	toluene	DMAP	77
17	CuCl	toluene	DABCO	78
18	-	toluene	-	0
19[c]	CuCl	toluene	-	69

[a]Reaction conditions: **1a** (0.48 mmol), **2a** (0.40 mmol), catalyst (10 mol %), solvent (4 mL), N_2 atmosphere, 80 °C. [b]Isolated yield based on substrate **2a**. [c]5 mol % of catalyst loading.

from hydrogen to a methyl or phenyl group, the reaction also worked to give the final products **3pa** and **3qa**, albeit in lower yield. It was interesting that a bromo group on the α-carbon of oxime acetate was also tolerated in the reaction, giving 55% yield of **3ra**. This was very useful for the further 4-functionalization of the generated product through various coupling reactions. When R^1 was an alkenyl or ester group, the desired product **3oa** or **3xa** was also obtained in 72% and 48% yield, respectively. Furthermore, cyclic ketoxime acetates led to the generation of polycyclic products **3sa** and **3ta** in moderate yield. However, when linear aliphatic ketoxime acetates were introduced to the reaction, the reaction was much more complicated. The oxime acetate derived from pinacolone yielded the desired product **3ua** in 58% yield, while pentan-3-one oxime acetate provided the isomerized products **3va′** and **3va″** having an exocyclic double bond in 28% and 17% yield, respectively. Pentan-2-one oxime acetate afforded the normal product **3wa** in 24% yield accompanied by the isomerized product **3wa′** in 20% yield. Next, the scope of α-sulfonamido malonates was examined. Regardless of either electron-rich or electron-deficient aryl groups of R^3, the reaction was performed well to give **3ab**−**3ad** in acceptable yield. Furthermore, when R^3 was an alkyl or *N*,*N*-dimethylamino group, the desired products **3ae** and **3af** also could be prepared in 76% and 61% yield, respectively.

Direct introduction of an amino group on the 3-carbon of 2-pyrrolones always needed several steps of transformations.[29] Using our developed method, a sulfonamido could be easily installed in the 3-position of 2-pyrrolone scaffolds. Encouraged by the good results obtained as discussed above, we turned our attention to *N*-aryl glycine esters. Ethyl *p*-tolylglycinate **4a** was selected as a model substrate to react with **1a** (Scheme 3, more conditions can be seen in Table S1 in the Supporting Information) under the standard conditions, and a very

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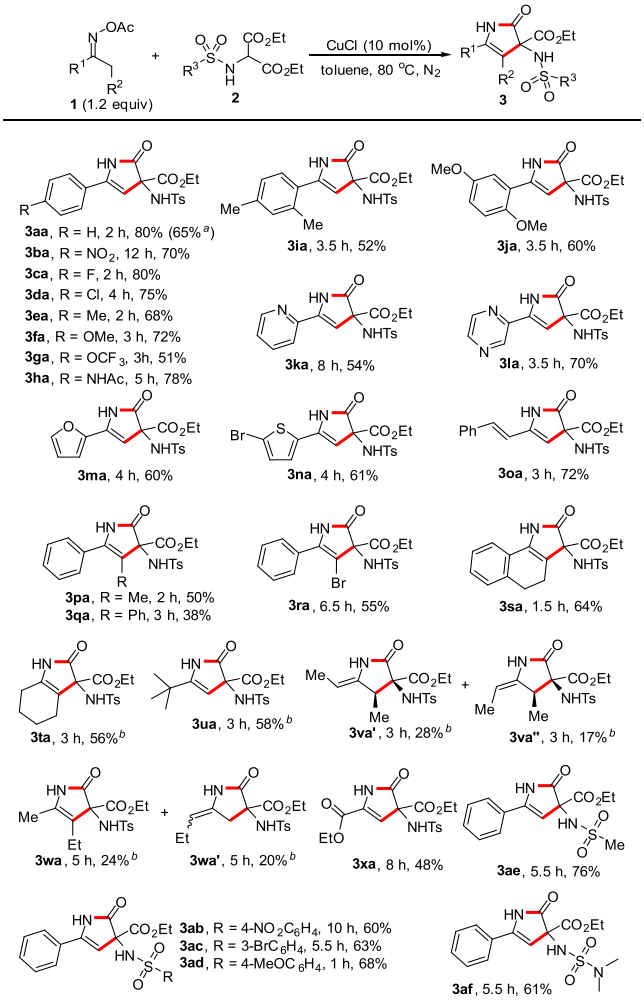
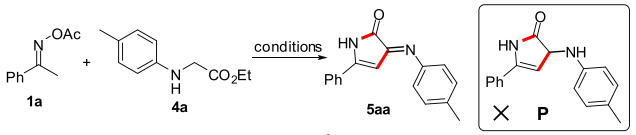
Scheme 2. Substrate Scope of Oxime Acetates and α-Sulfonamido Malonates



[a]Recrystallization yield with 5 mmol of **2a**. [b]1.5 equiv of **1w** was used.

Scheme 3. Reaction of Acetophenone Oxime Acetate with Ethyl *p*-Tolylglycinate 4a



CuCl (0.1 equiv), $PhCH_3$, 80 °C	0%
CuCl (0.1 equiv), K_2CO_3 (2 equiv), $PhCH_3$, 80 °C	11%
CuCl (2 equiv), K_2CO_3 (2 equiv), $PhCH_3$, 80 °C	23%
CuI (2 equiv), K_2CO_3 (2 equiv), $PhCH_3$, 80 °C	62%
CuI (2 equiv), K_2CO_3 (2 equiv), CH_3CN, 80 °C	70%
CuI (0.2 equiv), K_2CO_3 (1.2 equiv), DTBP (2.5 equiv), CH_3CN, 100 °C	68%

complex mixture was obtained. When K_2CO_3 was added to the reaction, a main product was formed in 11% yield, and most of the starting material remained unreacted. ^1H NMR analysis showed it was not the anticipated product **P** but the further oxidized product **5aa** (entry 2). It was worth noting that the C═N double bonds had a sole *E*-configuration through the NOESY analysis. This was quite different from the results previously reported by Chen's group, and therein, pyridines were obtained with the C−N bond cleavage of amines.[30] Obviously, an oxidative process was involved in the conversion of **P** to **5aa**. Then, we increased the amount of CuCl to 2 equiv. Although the yield was improved to 23%, it was still unsatisfactory (entry 3). Further screening of copper salts suggested that CuI was the most effective oxidant, giving **5aa** in 62% yield (entries 4−7). An extensive survey of solvents revealed that CH_3CN was the best solvent for the reaction, affording **5aa** in 70% yield (entries 8−11). To run the reaction with a catalytic amount of CuI, an external oxidant was added. When di-*tert*-butyl peroxide (DTBP) was added in combination with 0.2 equiv of CuI and 1.2 equiv of K_2CO_3, **5aa** was obtained in 32% yield after stirring at 80 °C for 12 h (entry 12). Increasing the temperature to 100 °C significantly improved the yield to 68% after 6 h (entry 13), indicating that a higher temperature was beneficial to the oxidation of low valent copper to high valent copper. The effect of $K_2S_2O_8$ was inferior to DTBP. Using *tert*-butyl peroxybenzoate as the oxidant resulted in the failure of reaction, and *tert*-butyl hydroperoxide only gave 9% of the product (entries 14−16). Using DMAP instead of K_2CO_3 led to a lower yield, while DABCO resulted in the failure of reaction (entries 17−18). When the amount of CuI was reduced to 0.1 equiv, the yield decreased to 57% (entry 19).

To evaluate the generality of this process, various oxime acetates were subjected to the reaction with **4a** (Scheme 4). Regardless of the functional groups at the *para*-positions, a large range of functional groups on the benzene ring, such as methoxyl, methyl, chlorine, fluoro, and nitro, were all tolerated, affording the desired 3-imine-4-pyrrolin-2-ones **5aa**−**5ha** and **5ka**. When polysubstituted oxime acetate including a cyclic keleton was used, this reaction occurred normally to furnish **5ia** or **5ja**. To further explore the scope of our method, various *N*-aryl-substituted glycine esters were subjected to the reaction. To our delight, methyl, methoxyl, and chloro groups on the phenyl ring had no influence on the reaction. However, when *N*-(4-nitrophenyl) glycine ester was subjected to the reaction, only a trace of product **5ad** was formed.

Due to the existence of an active imine C═N bond, we further studied the transformation of this kind of 4-pyrrolin-2-one **5** (Scheme 5). The reaction of indole, pyrrole, or 2,4-dimethylpyrrole with **5aa** catalyzed by NH_2SO_3H afforded the addition products **6**−**8** in 50−83% yields. When CH_3NO_2 and diethyl malonate were used as the nuceophiles, basic catalyst DBU was found to catalyze the reaction efficiently to afford **9** and **10** in 57% and 59% yield, respectively. Furthermore, the reaction of **5aa** with NIS provided the iodinated product **11**. However, when NIS was used instead of NBS, the product **12** was obtained in 50% yield via further addition with hypobromous acid.

Other amino acid ester derivatives were also evaluated in the two kinds of transformations (Scheme 5). For the reaction of **1a** with α-benzamido malonate **2g**, besides the desired product **13** (30%), compound **14** was also generated in 25% yield. When one of the ester groups of **2a** was replaced by a methyl group, no corresponding product **15** was formed, which indicated the significance of coexistence of the two ester groups. In the case of substrate **4**, changing the *N*-aryl group to an alkyl, tosyl, or benzamido group led to the failure of the reaction.

A possible mechanism is described in Scheme 6. Initially, the oxidative addition of the Cu^I to the N−O bond of the acetyl oxime **1** produces iminium radical **A** followed by the removal of Cu^{II}, which oxidizes **2a** and **4** to the corresponding imine intermediates **C** and **F**, respectively. Radical **A** reacts with Cu^I

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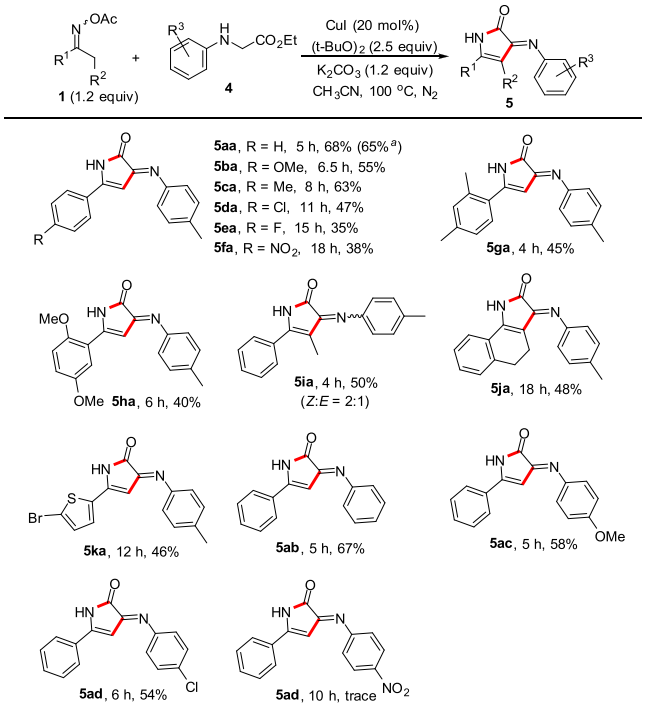
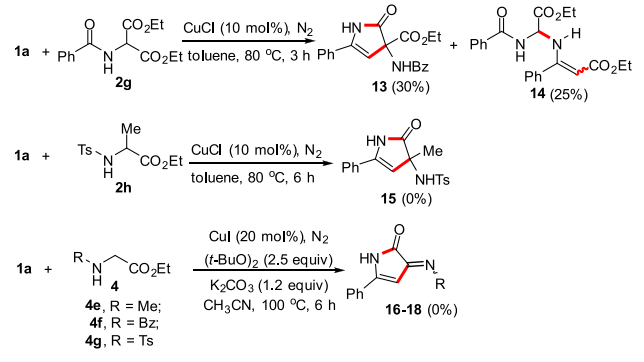
Scheme 4. Cu^{I}-Catalyzed Reaction of Oxime Acetates with *N*-Aryl Glycine Esters and the Further Transformation of 5aa



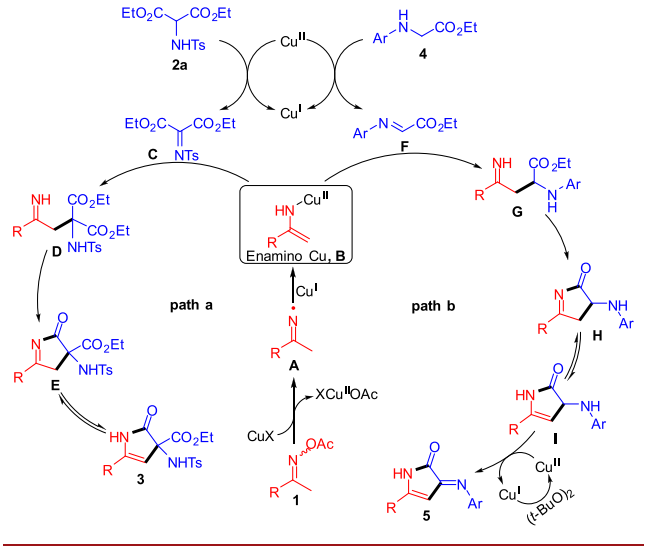
[a]Column chromatographic yield with 5 mmol of **4a**.

Scheme 5. Reaction of 1a with Other Amino Acid Ester Derivatives



to form an enamino-Cu^{II} intermediate **B**. In path a, nucleophilic addition of enamino-copper **B** to **C** followed by

Scheme 6. Plausible Mechanism



intramolecular cyclization generates **E**, which is tautomerized to **3aa**. In path **b**, addition of enamine-Cu^{II} **B** to **F** occurs to generate intermediate **G**. Subsequent intramolecular cyclization gives **H**, which equals **I**. The intermediate **I** is further oxidized by Cu(II) to furnish **5** with the release of Cu(I), which can be oxidized to Cu(II) by DTBP to enter the next cycle.

In summary, a novel convenient procedure for the synthesis of 3-sulfonamido/imino 4-pyrrolin-2-ones has been developed. In the presence of a catalytic amount of Cu^{I}, oxime esters act as an internal oxidant to oxidize α-amino acid esters to 1,2-dielectrophilic species, and a 1,3-dinucleophilic species was generated simultaneously. The following intermolecular nucleophilic cyclization affords 4-pyrrolin-2-ones. Readily available starting materials, mild conditions, and good functional compatibility make this method very attractive.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00870.

Experimental procedures, characterization data, and ^{1}H NMR and ^{13}C NMR spectra for all new products (PDF)

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Notes

The authors declare no competing financial interest.

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