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# Decarboxylative Alkynylation of α-Keto Acids and Oxamic Acids in Aqueous Media

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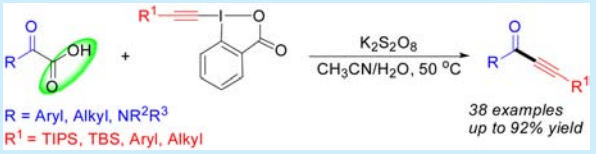
Supporting Information

**ABSTRACT:** A mild $K_2S_2O_8$ promoted decarboxylative alkynylation of α-keto acids and oxamic acids has been developed. This process features mild reaction conditions, a broad substrate scope, and good functional-group tolerance, therefore providing a new and efficient access to a wide range of ynones and propiolamides. Furthermore, this radical process could also be successfully applied to alkynylation of the $C_{sp^2}$−H bond in DMF with hypervalent alkynyl iodide reagents.




The decarboxylative cross-coupling reaction represents one of the most reliable methods to construct C−C and C−heteroatom bonds in current organic synthesis.[1] Compared with traditional cross-coupling reactions using sensitive organometallic reagents as sources of carbon nucleophiles, the decarboxylative reaction has proven to be a renewable and sustainable synthetic method to achieve these goals in view of the practical operation and easy availability of carboxylic acids.[2] Over the past decades, a number of decarboxylative reactions have been successfully developed for the synthesis of structurally diverse carbonyl compounds using α-keto acids as reactants.[3] In 1991, Minisci described the first silver-catalyzed homolytic acylation of heteroarenes with α-keto acids via a decarboxylative radical process.[3a] Since the pioneering palladium-catalyzed decarboxylative acylation reactions developed by Goossen and co-workers,[3b−d] the direct oxidative acylation of unactivated $C_{sp^2}$−H bonds has been particularly investigated in recent years.[3e−m] Subsequently, our group[4a−d] and others[4e−g] developed the radical-mediated tandem decarboxylative difunctionalization of unsaturated substrates with α-keto acids for the synthesis of various heterocycles and organofluorine compounds. Despite significant progress made in the formation of $C_{sp^2}$−$C_{sp^2}$ and $C_{sp^2}$−$C_{sp^3}$ bonds, the construction of the $C_{sp^2}$−$C_{sp}$ bond via transition-metal-free decarboxylative alkynylation of α-keto acids has not yet been reported and remains a challenging topic.[5]

In recent years, the hypervalent alkynyl iodide reagent has emerged as an efficient alkynylating reagent in organic synthesis.[6−10] In this field, Waser and co-workers have reported a series of the direct alkynylations of diverse substrates under transition-metal catalysis or metal-free conditions.[7] More recently, Rh(III)-catalyzed directed C−H alkynylation reactions have also been developed successfully by different research groups.[8] In addition, some excellent results using the alkynylated cyclic hypervalent iodine reagent as the reactant have also been described.[9] Recently, Li and co-workers developed an efficient Ag-catalyzed radical decarboxylative alkynylation of aliphatic carboxylic acids.[10a] However, compared with the above-mentioned synthetic procedures, the corresponding radical alkynylation reactions were still much less explored.[10] The above-mentioned elegant results, together with our continuing interest in decarboxylative coupling of α-keto acids,[3g,4a−d] prompted us to explore the direct decarboxylative alkynylation of α-keto acids with suitable alkynylating agents. Herein, we describe a new decarboxylative alkynylation of α-keto acids and oxamic acids under mild conditions for the synthesis of ynones and propiolamides, which are an important class of compounds in synthetic and natural product chemistry.[11]

Initially, the alkynyliodonium reagent 1-[(triisopropylsilyl)-ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, **2a**)[6] was chosen as a model substrate to optimize the reaction conditions for the direct decarboxylative alkynylation of phenylglyoxylic acid **1a**. To our delight, the reaction of **1a** and **2a** proceeded smoothly in the presence of 1.0 equiv of $K_2S_2O_8$ in $CH_3CN$/$H_2O$ (1:1) at 50 °C to afford the desired product **3a** in 74% yield even in the absence of the Ag(I) catalyst[3a,4,12] (Table 1, entry 1). A much better yield of **3a** was obtained by lowering the amount of $K_2S_2O_8$ to 0.7 equiv (entry 2). However, a further decrease of the oxidant amount resulted in a lower yield of **3a** (entry 3). After extensive screening of solvents and reaction temperatures, we found that the reaction in $CH_3CN$/$H_2O$ (1:1) at 50 °C gave the best result (entries 4−10). Other oxidants, such as $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$, were also effective for this transformation, while oxone and $PhI(OAc)_2$ were ineffective (entries 11−14). A control experiment revealed that $K_2S_2O_8$ was necessary for the success of this reaction (entry 15). Notably, this reaction could also be scaled up to 1 mmol, and the desired ynone **3a** was produced in 89% yield (entry 2).

To evaluate the generality of this decarboxylative alkynylation reaction, a wide range of α-keto acids **1** and hypervalent

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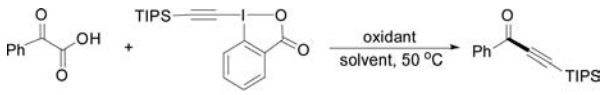
**Table 1. Optimization of the Decarboxylative Alkynylation of Phenylglyoxylic Acid**[a]

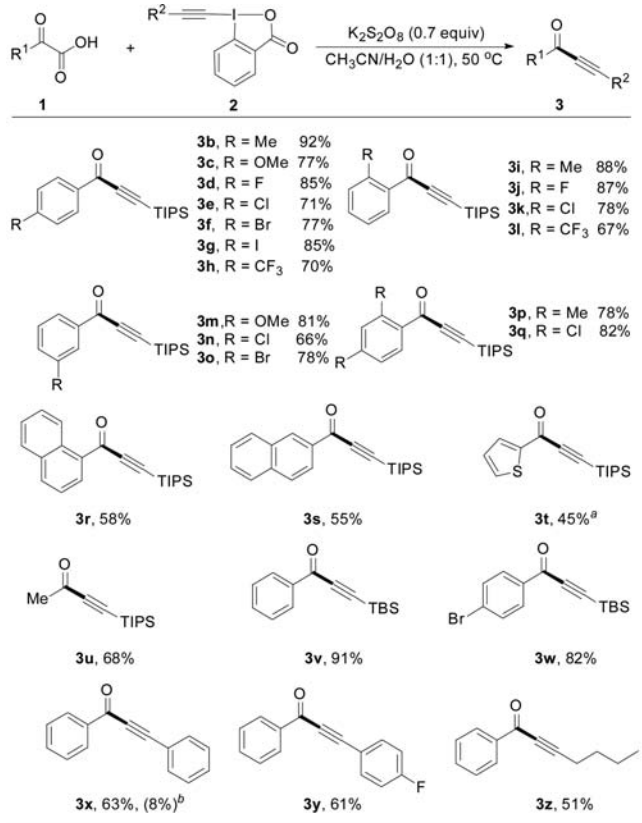



1a 2a 3a

| entry | oxidant (equiv) | solvent | yield (%)[b] |
|---|---|---|---|
| 1 | $K_2S_2O_8$ (1.0) | $CH_3CN/H_2O$ (1:1) | 74 |
| 2 | $K_2S_2O_8$ (0.7) | $CH_3CN/H_2O$ (1:1) | 86 (89)[c] |
| 3 | $K_2S_2O_8$ (0.5) | $CH_3CN/H_2O$ (1:1) | 59 |
| 4 | $K_2S_2O_8$ (0.7) | acetone/$H_2O$ (1:1) | 80 |
| 5 | $K_2S_2O_8$ (0.7) | AcOH/$H_2O$ (1:1) | 39 |
| 6 | $K_2S_2O_8$ (0.7) | DMF/$H_2O$ (1:1) | trace |
| 7 | $K_2S_2O_8$ (0.7) | $CH_2Cl_2/H_2O$ (1:1) | trace |
| 8 | $K_2S_2O_8$ (0.7) | $H_2O$ | 32 |
| 9[d] | $K_2S_2O_8$ (0.7) | $CH_3CN/H_2O$ (1:1) | 11 |
| 10[e] | $K_2S_2O_8$ (0.7) | $CH_3CN/H_2O$ (1:1) | 78 |
| 11 | $Na_2S_2O_8$ (0.7) | $CH_3CN/H_2O$ (1:1) | 83 |
| 12 | $(NH_4)_2S_2O_8$ (0.7) | $CH_3CN/H_2O$ (1:1) | 80 |
| 13 | oxone (0.7) | $CH_3CN/H_2O$ (1:1) | trace |
| 14 | $PhI(OAc)_2$ (0.7) | $CH_3CN/H_2O$ (1:1) | n.r.[f] |
| 15 | – | $CH_3CN/H_2O$ (1:1) | 0 |

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv), **2a** (0.20 mmol, 1.0 equiv), solvent (2 mL), oxidant, 50 °C, 24 h under $N_2$. [b]Yield of isolated product. [c]Yield on a 1 mmol scale is given in parentheses. [d]Room temperature. [e]At 80 °C. [f]n.r. = no reaction.

**Scheme 1. Scope of α-Keto Acids and Alkynylating Agents**




[a]10 mol % $AgNO_3$ was used. [b]Phenyl phenylethynyl sulfone was used as an alkynylating agent.

iodine reagents **2** were examined under the optimized reaction conditions (Scheme 1). In general, phenylglyoxylic acids having different substituents on the aromatic ring were all efficiently engaged in this reaction. As shown in Scheme 1, both electron-rich and -poor *p*-substituents on the phenylglyoxylic acid were compatible with the reaction conditions to give the desired products **3b–h** in good to excellent yields. Satisfactorily, phenylglyoxylic acids bearing an *ortho*-substituent, such as *o*-methyl, *o*-halo, and *o*-trifluoromethyl, also afforded the desired ynones **3i–l** in good yields, which indicated that the steric hindrance had little effect on this transformation. Furthermore, the *meta*-substituted phenylglyoxylic acids also worked well and gave the desired products **3m–o** in moderate to good yields. It is noteworthy that several functional groups such as ether, halo, and trifluoromethyl groups were tolerated well under the standard reaction conditions. In addition to the monosubstituted phenylglyoxylic acids, the sterically congested 2,4-disubstituted α-keto acids **1p** and **1q** also smoothly furnished the desired ynones **3p** and **3q** in 78% and 82% yields, respectively. The α- and β-naphthyloxoacetic acids **1r** and **1s** also produced the desired products **3r** and **3s**, albeit in somewhat low yields. The 2-thienylglyoxylic acid could also afford the corresponding product **3t** in 45% yield when 10% $AgNO_3$ was used as a catalyst. Furthermore, aliphatic α-keto acids, such as pyruvic acid, also provided the corresponding ynone **3u** in 68% yield. The silyl-substituted hypervalent alkynyl iodine reagent **2b** also afforded good yields of ynones **3v** and **3w**. Finally, aryl-EBXs and alkyl-EBX also worked with **1a** to afford the corresponding products **3x–z** in moderate yields. It should be noted that the phenyl phenylethynyl sulfone was less effective under this reaction system to furnish the desired product **3x** only in 8% yield. Moreover, the phenylethynyl phenyliodonium tosylate failed to produce the product **3x**.

Encouraged by the above results, we wished to apply this effective decarboxylative alkynylation reaction to the synthesis of other functionalized alkynes. To our delight, various oxamic acids could also undergo a similar process to give propiolamides in moderate yields under modified reaction conditions (Scheme 2). Treatment of *N*-phenyloxamic acid **4a** with **2a** in the presence of 1.0 equiv of $K_2S_2O_8$ in $CH_3CN/H_2O$ (1:1) at 50 °C for 24 h afforded the desired *N*-phenylpropiolamide **5a** in 51% yield.[13] Yet, oxamic acids with electron-donating and -withdrawing groups at the *para* or *ortho* positions of the aryl ring just led to the corresponding *N*-arylpropiolamides **5b–g** in poor yields, together with some unreacted starting materials recovered. We were delight to find that the yields of **5a–g** could be further improved to 51–74% by using 10% $AgNO_3$ as a catalyst. However, the *meta*-substituted oxamic acid **4h** resulted in only 29% yield. Oxamic acid **4i** bearing a bulky group also provided the desired amide **5i**, but in low yield. Moreover, *N*,*N*-disubstituted oxamic acids were also suitable substrates for this alkynylation reaction, the corresponding propiolamides **5j** and **5k** were isolated in 60% and 65% yields in the presence of catalyst, respectively. Unfortunately, when alkoxycarbonyl ketoacids such as monoethyl oxalate was used, no reaction occurred with **2a**. Interestingly, switching *N*,*N*-dimethyloxamic acid to *N*,*N*-dimethylformamide (DMF) as the $-CONMe_2$ source[4h,i,14] also led to the corresponding alkynylation products in moderate yields at 100 °C in the presence of $Ag(I)/K_2S_2O_8$ (eq 1).

To further explore the potential utilities of the alkynylation products, some transformations were conducted (for details see



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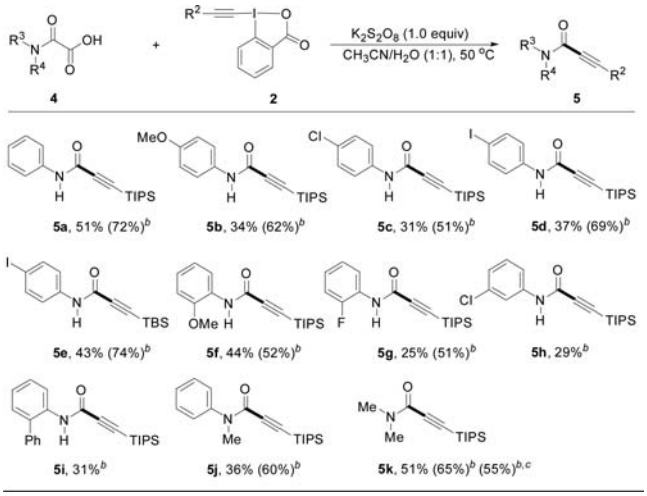
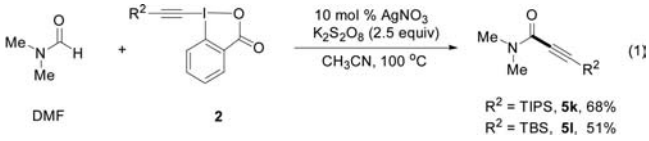
**Scheme 2. Scope of Oxamic Acids with 2**[a]

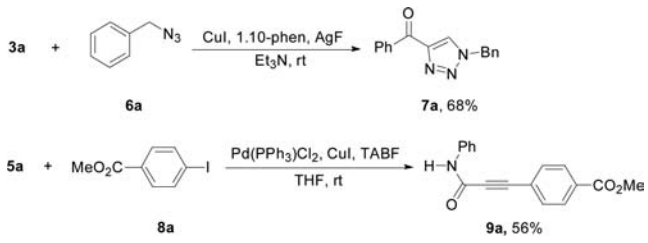



[a]Reaction conditions: **4** (0.24 mmol, 1.2 equiv), **2** (0.20 mmol, 1.0 equiv), $CH_3CN/H_2O$ (1:1, 2 mL), $K_2S_2O_8$ (0.20 mmol, 1.0 equiv), 50 °C, 24 h under $N_2$. [b]10 mol % $AgNO_3$ was used. [c]Yield on a 1 mmol scale is given in parentheses.




the Supporting Information). As shown in Scheme 3, the product **3a** could be easily converted to triazole **7a** via

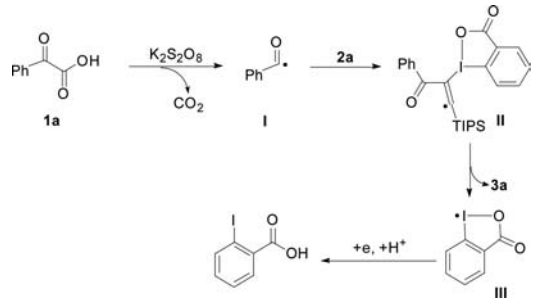
**Scheme 3. Derivatization of the Products 3a and 5a**




sequential desilylation and cycloaddition with benzyl azide. Furthermore, propiolamide **9a** was obtained in 56% yield through a one-pot desilylation/Sonogashira coupling of **5a** with methyl 4-iodobenzoate **8a**.

Finally, when radical scavengers, such as TEMPO and BHT, were added to the reaction system of **1a** and **2a**, only a trace amount of **3a** was detected (for details see the Supporting Information). These results indicated that the reaction probably proceeded via a free radical process. Based on our understanding of the oxidative decarboxylation of $\alpha$-keto acids[3a,4] and previous investigations,[10] a plausible mechanism was illustrated in Scheme 4. First, the oxidative decarboxylation of **1a** generates nucleophilic acyl radical **I** in the presence of $K_2S_2O_8$. Then, the radical **I** attacks the triple bond of hypervalent iodine reagent **2a** to produce the radical intermediate **II**.[10] Finally, the radical **II** undergoes $\beta$-elimination to afford the desired product **3a** along with the formation of 2-iodobenzoic acid, which was generated by a reduction−protonation of the benziodoxolonyl radical **III**. Given that only 0.7 equiv of $K_2S_2O_8$ was required in the cases of $\alpha$-keto

**Scheme 4. Proposed Mechanism**




acids, we presumed that the benziodoxolonyl radical **III** might also be participating in the generation of acyl radical **I** to fulfill the product formation.

In summary, we have developed a new $K_2S_2O_8$-promoted oxidative decarboxylative alkynylation of $\alpha$-keto acids under mild conditions. This process allows for the efficient preparation of functionalized ynones, which are important synthetic intermediates with diverse utilities in organic synthesis. Furthermore, the concept of this radical alkynylation could also be extended to oxamic acids and DMF, thus affording an alternative approach for the synthesis of propiolamides.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and spectroscopic data of new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01336.

## ■ AUTHOR INFORMATION

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### Notes

The authors declare no competing financial interest.

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