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**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.201701567

**Link to VoR:** <http://dx.doi.org/10.1002/adsc.201701567>

DOI: 10.1002/adsc.200((will be filled in by the editorial staff))


# Silver-Catalyzed Decarboxylative Couplings of Acids and Anhydrides: An Entry to 1,2-Diketones and Aryl-Substituted Ethanes

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Received: ((will be filled in by the editorial staff))

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**Abstract:** Silver-catalyzed oxidative decarboxylative coupling of carboxylic acids and anhydrides to produce 1,2-diketones and substituted ethanes was developed. This reaction allows the generation of acyl or alkyl radicals by decarboxylation of the corresponding  $\alpha$ -keto acids, alkyl acids and anhydrides, which are sequentially coupled to efficiently construct a new C-C bond. This reaction represents a carboxylic acid decarboxylative alternative that employs a radical termination strategy.

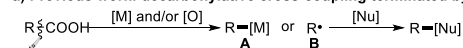
**Keywords:** silver; decarboxylation; coupling; carboxylic acids; 1,2-diketones

Carboxylic acids represents a class of common and essential chemical feedstocks that are widely utilized for the construction of complex molecular structures in synthesis. In recent years, the decarboxylative coupling strategies for the transformations of carboxylic acids to forge new chemical bonds to carbon atoms have been extensively investigated, since, compared to traditional halide electrophiles, carboxylic acids are more ideal and greener, because they release CO<sub>2</sub> gas as a byproduct.<sup>[1,2]</sup> Generally, carboxylic acids undergo decarboxylation with a metal and/or an oxidant to release CO<sub>2</sub> and form a C-M species (**A**)<sup>[1]</sup> or a carbon-centered radical (**B**),<sup>[2]</sup> which sequentially react with nucleophiles to form new chemical bonds to carbon atoms and increase molecular complexity (Scheme 1a). However, to the best of our knowledge, examples involving decarboxylative homocouplings of carboxylic acids via a two-radical-coupling strategy have never been reported.<sup>[3]</sup>

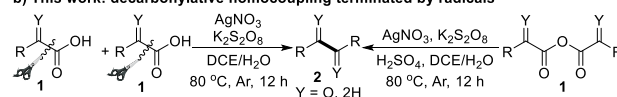
Silver catalysis has emerged as one of the most important technologies in chemical synthesis.<sup>[2d,4]</sup> In particular, silver-catalyzed oxidative radical coupling reactions have attracted increasing interest recently because their advent has inspired new methodologies. Among these methodologies, silver-catalyzed oxidative decarboxylative couplings of carboxylic

acids, including common alkyl acids, aryl acids and  $\alpha$ -keto acids, have also been well studied along with all the available variations involving the use of nucleophilic terminators as well.<sup>[2d,5]</sup> Thus, new general and efficient alternatives to oxidative decarboxylative couplings of carboxylic acids that avoid the use of the nucleophilic terminators would be desirable and would inspire the rapid development of new silver catalysis<sup>[6]</sup> and radical methodologies. Herein, we report a new strategy for producing 1,2-diketones and substituted ethanes by silver-catalyzed oxidative decarboxylative homocouplings of carboxylic acids, including  $\alpha$ -keto acids and alkyl acids. The coupling is achieved by the generation of acyl or alkyl radicals from the corresponding carboxylic acids. This reaction enables the formation of a new C-C bond via sequential decarboxylation and two radical coupling, and represents a new silver-catalyzed oxidative decarboxylative transformations of carboxylic acids terminated by radicals. Moreover, this reaction is applicable to decarboxylative couplings of anhydrides. Notably, the products, 1,2-diketones, are of great importance in synthesis, especially in the preparation of diverse pharmaceuticals and functional materials.<sup>[7]</sup>

a) Previous work: decarboxylative cross-coupling terminated by nucleophiles



b) This work: decarboxylative homocoupling terminated by radicals



**Scheme 1.** Decarboxylation of Acids and Anhydrides.

Our investigation commenced with the decarboxylative homocoupling of 2-oxo-2-phenylacetic acid (**1a**) (Table 1). A catalytic system comprising 20 mol% of AgNO<sub>3</sub> and 3 equiv of

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$K_2S_2O_8$  in a mixture of  $CH_2ClCH_2Cl$  (DCE) and  $H_2O$  (v/v = 2:1) at 80 °C afforded the desired benzil **2a** in 73% yield (entry 1). The results showed that the silver catalysts and the oxidants played a crucial role in the reaction, as the reaction did not proceed in the absence of either the silver catalyst or the oxidant (entries 2 and 8). A lower loading of  $AgNO_3$  (10 mol%) diminished the yield (entry 3), but additional  $AgNO_3$  (30 mol%) provided no improvement beyond the results observed with 20 mol% of  $AgNO_3$  (entry 4). Using  $Ag_2SO_4$ ,  $AgSbF_6$  or  $Ag_2O$  as the catalysts instead of  $AgNO_3$  led to decreased yields (entries 5-7). However, using either more or less  $K_2S_2O_8$  had a negative effect on the reaction outcome (entries 9 and 10). Two other oxidants, oxone and TBHP, exhibited lower reactivities than  $K_2S_2O_8$  (entries 11 and 12). It was noted that the amount of  $H_2O$  present had a substantial influence on the yield probably because the presence of  $H_2O$  promotes the dissolution of  $K_2S_2O_8$  (entries 13-15). Other media, such as  $CH_2Cl_2/H_2O$ ,  $MeCN/H_2O$  and  $EtOAc/H_2O$ , were inferior to  $CH_2ClCH_2Cl/H_2O$  (entries 16-18). Screening of reaction temperatures revealed that running the reaction at 80 °C provided the best results (entries 1 and 19-20). Notably, the reaction was successfully scaled up to 1 mmol of 2-oxo-2-phenylacetic acid (**1a**), and the reaction provided benzil **2a** in good yield (entry 21).

**Table 1.** Optimization of the Reaction Conditions<sup>[a]</sup>

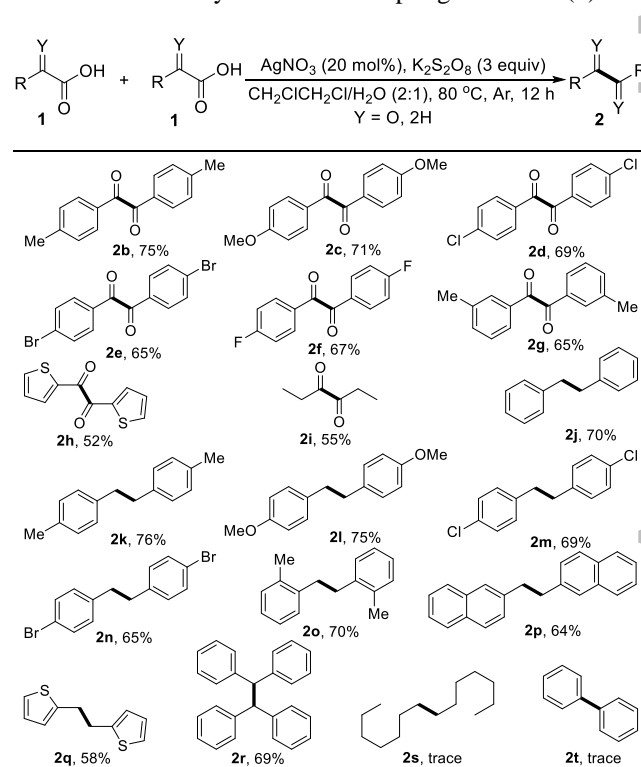
Entry	Variation from the optimal conditions	Yield [%] <sup>[b]</sup>
1	none	73
2	Without $AgNO_3$	trace
3	$AgNO_3$ (10 mol%)	59
4	$AgNO_3$ (30 mol%)	71
5	$Ag_2SO_4$ instead of $AgNO_3$	27
6	$AgSbF_6$ instead of $AgNO_3$	28
7	$Ag_2O$ instead of $AgNO_3$	20
8	Without $K_2S_2O_8$	trace
9	$K_2S_2O_8$ (2 equiv)	65
10	$K_2S_2O_8$ (5 equiv)	64
11	Oxone (3 equiv)	35
12	TBHP (3 equiv)	trace
13	Without $H_2O$	10
14	$CH_2ClCH_2Cl/H_2O$ (3:1)	51
15	$CH_2ClCH_2Cl/H_2O$ (1:1)	57
16	$CH_2Cl_2$ instead of $CH_2ClCH_2Cl$	45
17	$MeCN$ instead of $CH_2ClCH_2Cl$	42
18	$EtOAc$ instead of $CH_2ClCH_2Cl$	23
19	At 60 °C	65
20	At 100 °C	71
21 <sup>[c]</sup>	none	70

<sup>[a]</sup> Reaction conditions: **1a** (0.2 mmol),  $AgNO_3$  (20 mol%),  $K_2S_2O_8$  (3 equiv),  $CH_2ClCH_2Cl$  (2 mL),  $H_2O$  (1 mL), argon, 80 °C and 12 h. <sup>[b]</sup> Isolated yield. <sup>[c]</sup> **1a** (1 mmol) for 24 h.

We next applied the optimal reaction conditions to the decarboxylative homocouplings of a wide range of acids, namely,  $\alpha$ -keto acids **1b-1i**, 2-arylacetic acids **1j-r**, heptanoic acid (**1s**) and benzoic acid (**1t**) (Scheme 2). Gratifyingly, the optimal conditions were compatible with various 2-oxo-2-arylacetic acids **1b-1g**, and several substituted aryl groups, such as 4- $MeC_6H_4$ , 4- $MeOC_6H_4$ , 4- $ClC_6H_4$ , 4- $BrC_6H_4$ , 4- $FC_6H_4$ , 3- $MeC_6H_4$  and thiophen-2-yl (products **2b-g**), were well tolerated. In addition, the electronic and steric properties of the aryl groups has a slight impact on the yields. Electron-rich  $MeC_6H_4$ -substituted acids **1b** and **1g**, for example, delivered the corresponding 1,2-diketones **2b** and **2g** in 75% and 65% yields, respectively, whereas weakly electron-deficient  $FC_6H_4$ -substituted acid **1f** was converted into 1,2-diketone **2f** in 67% yield. Using heteraryl-containing acid, 2-(thiophen-2-yl)acetic acid **1h** was reacted with  $AgNO_3$  and  $K_2S_2O_8$ , corresponding product **2h** was produced in moderate yield. Notably, aliphatic 2-oxobutanoic acid (**1i**) was a suitable substrate for this reaction and provided **2i** in a synthetically useful yield.

Gratifyingly, this decarboxylative homocoupling methodology is applicable to 2-aryl-substituted acetic acids. Treatment of 2-phenylacetic acid (**1j**) with  $AgNO_3$  and  $K_2S_2O_8$  smoothly afforded

**Table 2.** Decarboxylative Homocouplings of Acids (**1**)<sup>[a]</sup>

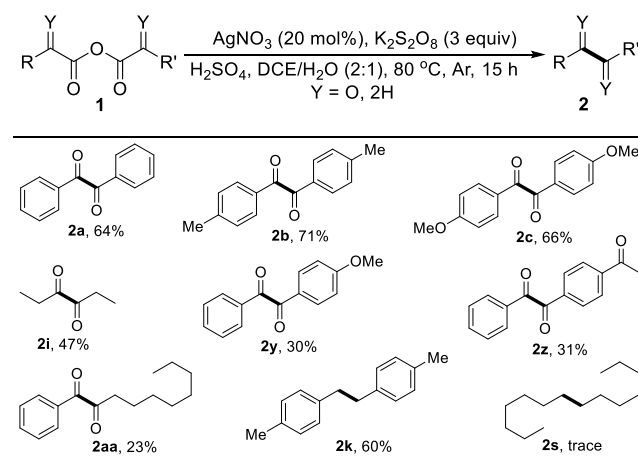


<sup>[a]</sup> Reaction conditions: **1** (0.2 mmol),  $AgNO_3$  (20 mol%),  $K_2S_2O_8$  (3 equiv),  $CH_2ClCH_2Cl$  (2 mL),  $H_2O$  (1 mL), argon, 80 °C and 12 h.

1,2-diphenylethane (**2j**) in 76% yield. A number of substituents, namely, Me, MeO, Cl and Br, on the 2-position of the aryl ring were perfectly tolerated and produced corresponding 1,2-diarylethanes **2k-o** in 67%-76% yields. 2-(Naphthalen-1-yl)acetic acid (**1p**) and 2-(thiophen-2-yl)acetic acid (**1q**), both were both competent substrates and afforded **2p-q** in reasonable yields. We were pleased to find that 2,2-diphenylacetic acid (**1r**), a secondary acid, was efficiently converted into the useful compound 1,1,2,2-tetraphenylethane (**2r**). Unfortunately, the other common alkyl and aryl acids, such as heptanoic acid (**1s**) and benzoic acid (**1t**), were not reactive under these conditions. The reason for the failure of aliphatic acids, such as heptanoic acid, might be attributed to the fast H-abstraction of ordinary primary alkyl radicals.

As shown in Table 3, a variety of anhydrides were employed in this decarboxylative coupling reaction. In the presence of AgNO<sub>3</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> (two drops), 2-oxo-2-phenylacetic anhydride (**1u**) was successfully converted into benzil (**2a**) in 64% yield. Likewise, other anhydrides, including 2-oxo-2-(*p*-tolyl)acetic anhydride (**1v**), 2-(4-methoxyphenyl)-2-oxoacetic anhydride (**1w**) and 2-oxobutanoic anhydride (**1x**), were well-tolerated and generated corresponding products **2b-c** and **2i** in good yields. Using unsymmetric anhydrides **1y-aa** afforded unsymmetric 1,2-diketones **2y-aa**, albeit in low yields. The reaction of 2-(4-methoxyphenyl)acetic anhydride (**1ab**) smoothly afforded **2k** in 60% yield. However, heptanoic anhydride (**1ac**) was inert in the reaction (product **2s**).

**Table 3.** Decarboxylative Coupling of Anhydrides (**1**)<sup>[a]</sup>

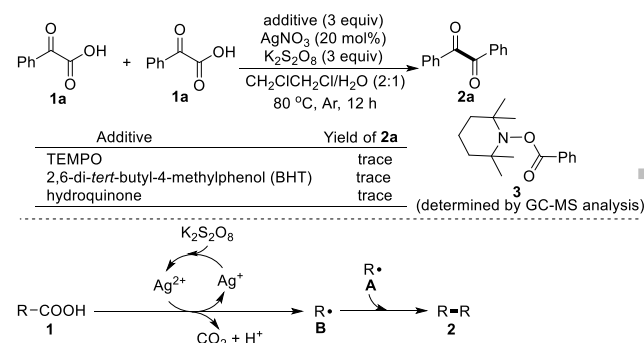


<sup>[a]</sup> Reaction conditions: **1** (0.2 mmol), AgNO<sub>3</sub> (20 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3 equiv), H<sub>2</sub>SO<sub>4</sub> (two drops, 3 N), CH<sub>2</sub>ClCH<sub>2</sub>Cl (2 mL), H<sub>2</sub>O (1 mL), argon, 80 °C and 15 h.

The control experiments outlined in Scheme 2 showed that the decarboxylative homocoupling of acid **1a** was impeded by the presence of a stoichiometric amount of a radical inhibitor, including TEMPO, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and hydroquinone. These results support the theory that

this decarboxylative homocoupling reaction is a radical process.

Consequently, the mechanism of this decarboxylative coupling reaction was proposed (Scheme 2).<sup>[4-6,8]</sup> Initially, the active Ag<sup>2+</sup> species is generated by the oxidation of the Ag<sup>+</sup> species with persulfate. Subsequently, acid **1** undergoes single electron oxidative decarboxylation with the active Ag<sup>2+</sup> species to afford the radical intermediate **B** and regenerate the Ag<sup>+</sup> species.<sup>[4,5]</sup> Finally, homocouplings of two equivalents of radical intermediate **B**<sup>[8]</sup> produces the desired product **2**.



**Scheme 2.** Control Experiments and Possible Reaction Mechanism.

In summary, we have developed a facile protocol for the synthesis of 1,2-diketones and aryl-substituted ethanes via silver-catalyzed oxidative decarboxylative couplings of carboxylic acids or anhydrides. By employing AgNO<sub>3</sub> as the catalyst and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the oxidant, a wide range of  $\alpha$ -keto acids, 2-aryl-substituted acetic acids and anhydrides efficiently underwent the oxidative decarboxylative homocoupling reaction to afford the corresponding 1,2-diketones and aryl-substituted ethanes. Importantly, this technology utilizes a radical to terminate the decarboxylative coupling, thus offering a facile entry to elongating a carbon chain.

## Experimental Section

### General Considerations:

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solvents on an NMR spectrometer using TMS as the internal standard. LRMS was performed on a GC-MS instrument.

### Typical Experimental Procedures

**Typical Experimental Procedure for Silver-Catalyzed Decarboxylative Couplings of Acids:** To a Schlenk tube were added acids **1** (0.2 mmol), AgNO<sub>3</sub> (20 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3 equiv), CH<sub>2</sub>ClCH<sub>2</sub>Cl (2 mL) and H<sub>2</sub>O (1 mL). Then, the tube was charged with argon and was stirred at 80 °C for 12 h until complete consumption of the starting material as determined by TLC and/or GC-MS analysis. After the

reaction was finished, the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The aqueous phase was extracted with ethyl acetate and then washed with saturated NaCl. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated, and then purified by column chromatography (petroleum ether/ethyl acetate, v/v=20/1) to afford the target products **2**.

## Acknowledgements

We thank the Natural Science Foundation of China (Nos. 21625203 and 21472039) and the Jiangxi Province Science and Technology Project (Nos. 20171ACB20015 and 20165BCB18007) for financial support.

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## COMMUNICATION

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