



Oxidative decarboxylation of arylacetic acids in water: One-pot transition-metal-free synthesis of aldehydes and ketones



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ARTICLE INFO

Article history:

Received 13 May 2017

Accepted 4 June 2017

Available online 14 June 2017

Keywords:

Transition-metal-free

Water

Persulfate

One-pot synthesis

Decarboxylation

ABSTRACT

One-pot transition-metal-free synthesis of aromatic aldehydes and ketones via oxidative decarboxylation of arylacetic acids in water is developed. Protocol relies on the direct decarboxylation of sp^3 -hybridized carbon in water without any over oxidation into carboxylic acids with minimal waste. Reaction mechanism is investigated and application of this protocol is demonstrated on a gram scale.

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Introduction

Aldehydes and ketones are very important class of compounds and they have been used extensively in wide areas of chemical synthesis.¹ Evidently, the effort towards the quick and short synthesis of aldehydes and ketones always has been desirable. Traditional synthesis of aldehydes and ketones rely on activating the carboxylic acid into a Weinreb amide² or into an acyl halide³ with subsequent nucleophilic attack with hydrides or organometallic species. One-step synthesis of ketones starting from carboxylic acids can be achieved using excess of organolithium reagents; however formation of tertiary alcohols is unavoidable.⁴ These harsh conditions can lead to the erosion of stereochemical purity thus leading to partial racemization.⁵ Nevertheless, efforts have been made to improvise the existing methods. Cyanocuprates have been explored to convert the carboxylic acids directly into ketones.⁶ Quick and efficient cleavage of carbon-carbon bond is one of the most important challenges in organic synthesis.⁷ The selective cleavage of C–C σ bond has greatly attracted the attention of researchers in the recent times due to its inert nature. Undoubtedly, development of an efficient protocol for the selective cleavage of C–C σ bond is a great challenge and still much to be explored. Transition metal catalyzed decarboxylation via C–C bond cleavage has been gaining a great importance due to its significant role in decarboxylative reactions.⁸ Elegant and valuable protocols are developed in this area for making carbon-carbon and

carbon-heteroatom bonds starting from carboxylic acids and by cleaving the C–C bond to carboxylate group.⁹ Also, decarboxylation reaction procedures are usually done at neutral reaction conditions and importantly carbon dioxide liberated as a sole non-toxic by-product. Transition metal catalyzed decarboxylation at sp^2 -hybridized carbon is mostly explored in the literature and more strikingly, decarboxylation at sp^3 -hybridized carbon to introduce a functional group is relatively rare and challenging.¹⁰ Transition metal catalyzed synthesis of aldehydes, ketones and amides via oxidative decarboxylation has been explored very recently.^{11,12} Reactivity of cuprous salt was explored for the novel synthesis of aldehydes from methyl ketones in presence of oxygen.¹³ Recently, Song and co-workers demonstrated the ability of cupric salts for the aerobic oxidative decarboxylation at sp^3 -hybridized carbon to afford aldehydes, ketones¹¹ and amides¹² at high temperatures. Decarboxylative non-aerobic oxidation of phenyl acetic acid to benzaldehyde was described by using cupric salts at high temperature and pressure thus mimicking the geochemically relevant conditions.¹⁴ All of these protocols rely on transition metal, viz. copper for catalyzing the transformation.¹⁵ However, there are only countable protocols for the oxidative decarboxylation of aryl carboxylic acids under transition-metal-free conditions. Earlier, decarboxylation of carboxylic acids to aldehydes and ketones were achieved by using tetrabutylammonium periodate in 1,4-dioxane under refluxing condition, combination of iron(III)/manganese(III) tetraphenylporphyrins and tetrabutylammonium periodate, and (diacetoxyiodo)benzene/ NaN_3 .^{16,17} Thus development of more easier, practical and non-hazardous protocol for the synthesis of aldehydes and ketones via oxidative decarboxylation under

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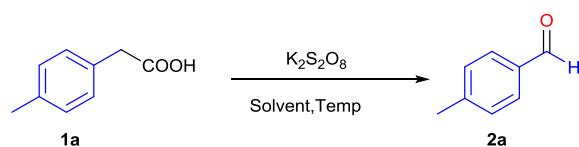
transition-metal-free conditions is highly desirable. There are ambiguities in defining a true 'green method'. However, some of the most accepted guiding principles such as minimal waste, higher mass productivity lower E-factor, non-toxicity etc define the greener methods. Practical, efficient and highly selective transition-metal-free transformations using environmentally benign, less expensive and readily available reagents are gaining a great importance for the last few years.¹⁸ As a part of our ongoing efforts to develop transition metal free protocols,¹⁹ we herein, report an oxidative decarboxylative strategy for the direct and clean synthesis of aldehydes and ketones without over oxidation into carboxylic acids in water with a minimal waste and lower E-factor. This simple protocol uses potassium persulfate as a reagent and makes the novel use of it for the synthesis of aldehydes and ketones starting from arylacetic acids.

We commenced our initial work with 4-methyl phenylacetic acid **1a** with $K_2S_2O_8$ as a model reaction (Table 1). Attempted reaction of **1a** with $K_2S_2O_8$ (2 equiv.) in CH_3CN/H_2O (1:1) at room temperature (both in air and inert condition) did not work even after prolonged reaction condition (entry 1, Table 1). Interestingly, when the reaction was carried at elevated temperature (80 °C), to our delight, the desired product, 4-methylbenzaldehyde **2a** was formed in 75% isolated yield (Table 1, entry 2) in 12 h. With this result in hand, further the reaction was screened in different solvent conditions. However, the reaction was sluggish in CH_3CN and DCE (entries 4, 6) and afforded only trace amount of desired product **2a**. However, the reaction in DCE/ H_2O at 80 °C afforded the desired product in 60% yield (entry 7). Interestingly, the model reaction worked efficiently only in water at 80 °C affording the desired product 4-methyl benzaldehyde **2a** in 75% yield (entry 8). Gratifyingly, with the elevated temperature (90 °C) under aerial condition reaction afforded the compound **2a** in excellent yield of 85% (entry 9). PIDA, PIFA and Oxone were found to be ineffective reagents for the desired transformation (entries 10–12). Attempts to lower the reaction temperature resulted in lower yield with

incomplete conversion of the starting material (entry 13). Reactions under oxygen or open air atmosphere did not change the course of the reaction and also did not have any significant effect on yield or reaction time (entries 9, 14). Reaction did not work in the absence of potassium persulfate (entry 15). After extensive screening of solvents and temperature optimum reaction condition was emerged as 4-methylphenyl acetic acid **1a** (1 equiv.), $K_2S_2O_8$ (2 equiv.) at 90 °C in water under aerial atmosphere (entry 9, Table 1) in 12 h. It is also important to note that persulfates are very popular for their ability to oxidize variety of contaminants in ground water via 'in situ chemical oxidation' (ISCO).²⁰ Persulfates are known to be benign, eco-friendly or green and low cost reagent.²¹

Encouraged by the initial success and with an optimized reaction condition in hand; we explored the substrate scope of the method. Under optimal reaction conditions arylacetic acids (**1a–1o**) possessing the electron-donating group as well as electron withdrawing groups reacted smoothly by affording the corresponding aldehydes (**2a–2o**) in moderate to good yields (Scheme 1). 1-Naphthylacetic acid **1p** reacted smoothly and gave the corresponding naphthaldehyde **2p** in 80% yield. Similarly, the heteroaromatic acid such as 2-thienyl acetic acid **1q** under reaction conditions afforded the 2-thienyl carboxylaldehyde (**2q**). α -Substituted phenyl acetic acids (**1r–1w**) under optimal reaction conditions afforded the corresponding ketones (**2r–2w**) in excellent yields (86–92%). The anti-inflammatory drug, ibuprofen **1u** afforded the corresponding ketone²² **2u** in excellent yield as well. Interestingly, the amino acid phenyl glycine **1x** afforded benzaldehyde **2d** instead of anticipated amide. Probably, imine might have formed during the course of reaction, which upon hydrolysis resulted in **2d**. The position of the substituents on the ring had no significant and noticeable effect on reaction rate and yields. Functional group such as hydroxyl, chloro, bromo, methoxy and nitro were well tolerated. However, unfortunately, attempted reac-

Table 1
Optimization of the reaction conditions.^a



Entry	Reagent	Solvent	Temp (°C)	Atm	Yield ^b (%)
1	$K_2S_2O_8$	CH_3CN/H_2O (1:1)	rt	Air	NR
2	$K_2S_2O_8$	CH_3CN/H_2O (1:1)	80	Air	75
3	$K_2S_2O_8$	CH_3CN	Reflux	Air	Trace
4	$K_2S_2O_8$	CH_3CN	Reflux	O_2	12
5	$K_2S_2O_8$	MeOH	Reflux	Air	NR
6	$K_2S_2O_8$	DCE	90	O_2	Trace
7	$K_2S_2O_8$	DCE/ H_2O (1:1)	80	Air	60
8	$K_2S_2O_8$	H_2O	80	Air	75
9	$K_2S_2O_8$	H_2O	90	Air	85
10	PIDA	H_2O	90 ^c	Air	27
11	PIFA	H_2O	90 ^c	Air	21
12	Oxone	H_2O	90 ^c	Air	15
13	$K_2S_2O_8$	H_2O	50	Air	20
14	$K_2S_2O_8$	H_2O	90	O_2	83
15	–	H_2O	90	Air	–

Bold values correspond to the optimum reaction conditions.

^a Reaction conditions: 4-methylphenyl acetic acid **1a** (1 equiv.), potassium persulfate (2 equiv.), solvent (2 mL) under corresponding atmosphere for 12 h.

^b Isolated yield after purification by column chromatography.

^c Reactions did not work at rt.

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