Oxidative Decarboxylation of Arylacetic Acids: Novel Approach to the Synthesis of Aryl Aldehydes and Ketones

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ABSTRACT

Oxidation and decarboxylation are among the most important processes in organic synthesis. The combination of these two fundamental processes provides a novel synthetic strategy, that is, oxidative decarboxylation. Over the past few years, considerable attention has been focused on such an attractive research arena. This review offers an overview of the utility of oxidative decarboxylation in the synthesis of various aryl aldehydes and ketones from the corresponding arylacetic acids. The review is divided into three major sections. The first section focuses exclusively on metal-catalyzed reactions. The second section will discuss metal-free approaches. The third will cover photoredox-catalyzed decarboxylative oxidations. Literature has been surveyed from the year 1980 to 2022.
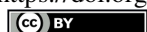
1. Introduction

Aldehydes and ketones are the simplest and most important carbonyl compounds which found in many pharmaceutical, bioactive molecules, and natural products (Scheme 1) [1, 2]. In addition, they are recognized as versatile synthetic precursors of fundamental functional groups, such as thioesters, alcohols, amines, imines, enamines [3]. The conventional synthetic approach to aldehydes and ketones rely on activating the carboxylic acid into a Weinreb amide [4] or into an acyl halide [5] with subsequent nucleophilic attack with hydrides or organometallic species. However, requirement to the very low temperature, toxic organometallic reagent and/or inert atmosphere limited the utility of these methods. On the other hand, the direct one-pot synthesis of these classes of carbonyl compounds from carboxylic acids are also demonstrated, even though such a process
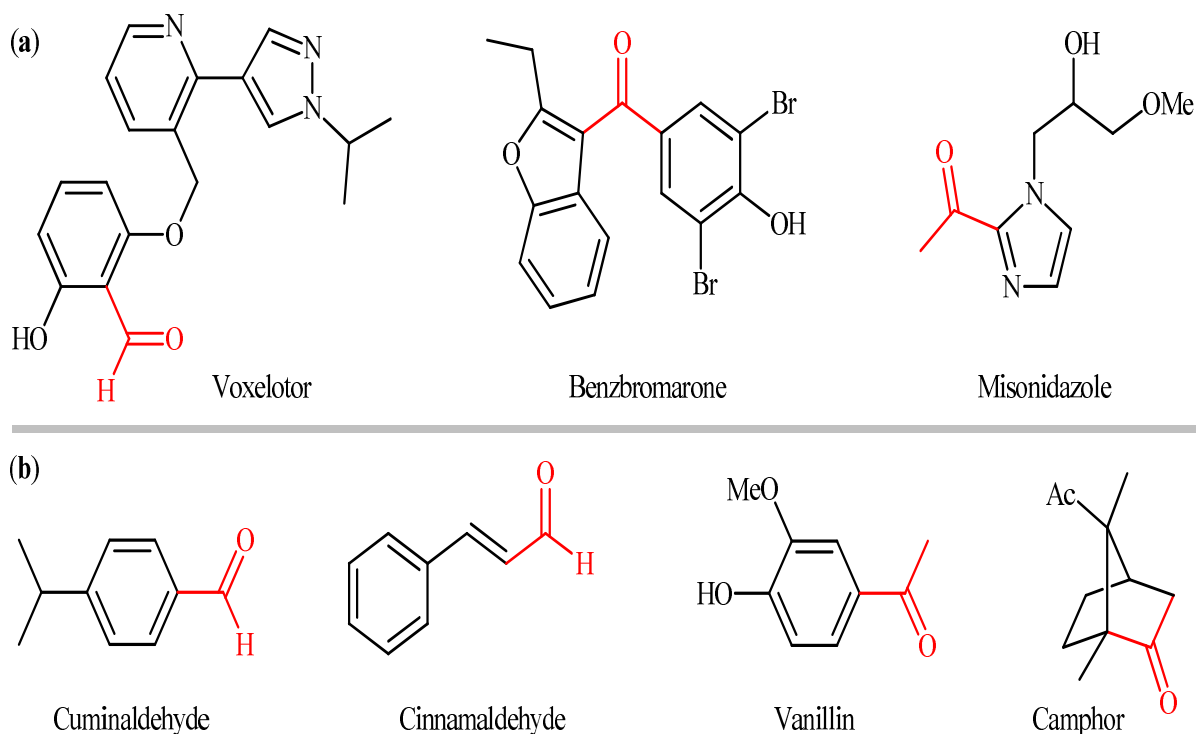
is difficult and formation of side-products is unavoidable [6]. Oxidative decarboxylation, the combination of oxidation and carbon dioxide removal, has attracted much attention in recent years and has emerged as one of the major themes in organic synthetic chemistry [7]. In this regard, since its first description in 1980, there has been much research interest in the synthesis of synthetically and biologically important aryl aldehydes and ketones from the respective arylacetic acids. Beside simplicity, broad substrate scope and easily accessible starting materials can be considered as the advantages of this appealing synthetic process. Although numerous studies have investigated on this synthetic strategy over the past few years, to the best of our knowledge, a comprehensive review has not presently appeared on this research field in literature. In continuation of previous review works on modern organic synthesis [8], in this review, we will highlight

(a)

Voxelotor

Benzbromarone

Misonidazole

(b)

Cuminaldehyde

Cinnamaldehyde

Vanillin

Camphor

Scheme 1. (a) Selected examples of Aldehyde and ketone containing drugs; (b) Aldehyde and ketone containing molecules isolated from natural sources.
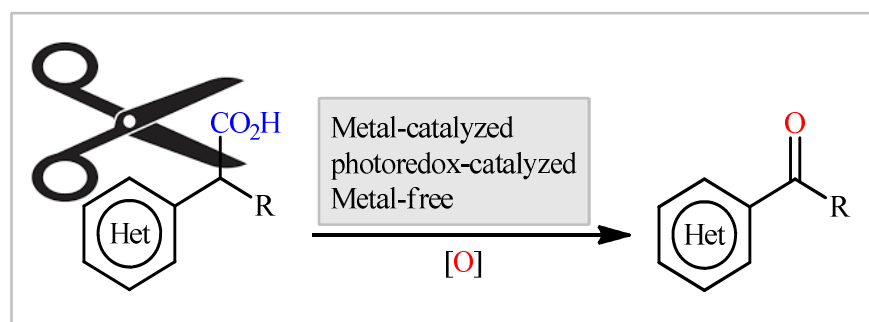
Fig 1. Oxidative decarboxylation of arylacetic acids.

the most significant advances on this chemistry (Fig 1), which will be helpful in the development of improved methods for the preparation of biologically important carbonyl compounds.

2. Metal-free reactions

Drawing inspiration from the preliminary work by Santaniello's research group on the synthesis of a small series of aromatic aldehydes and ketones 2 through the oxidative decarboxylation of respective arylacetic acids 1 by means of tetrabutylammonium periodate (TBAPI)

in refluxing dioxane (Scheme 2a) [9], Telvekar and Sasane developed a mild and convenient methodology for the high yielding synthesis of aryl dehyde and ketone derivatives 4 from the corresponding arylacetic acids 3 employing NaN_3 as the catalyst and the hypervalent iodine reagent, phenyliodine(III) diacetate (PIDA) as an oxidant [10]. The reactions were carried out in MeCN at room temperature, tolerated various electron-donating and –withdrawing functionalities, and provided the desired carbonyl compounds within the minutes (Scheme 2b). However, aliphatic carboxylic acids were incompatible in the reaction.

Under the identical conditions, an α-hydroxyphenylacetic acid was also examined and the desired aldehyde was obtained in excellent yield. Interestingly, when α-amino aryl carboxylic acids wer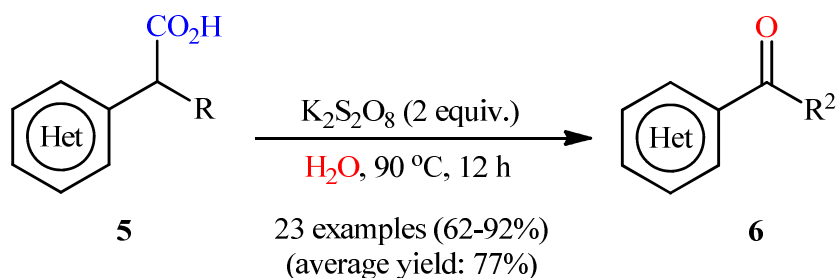e subjected to the reaction, the corresponding nitriles were isolated as the sole products. Unfortunately, the authors did not propose a reaction mechanism for the transformation.
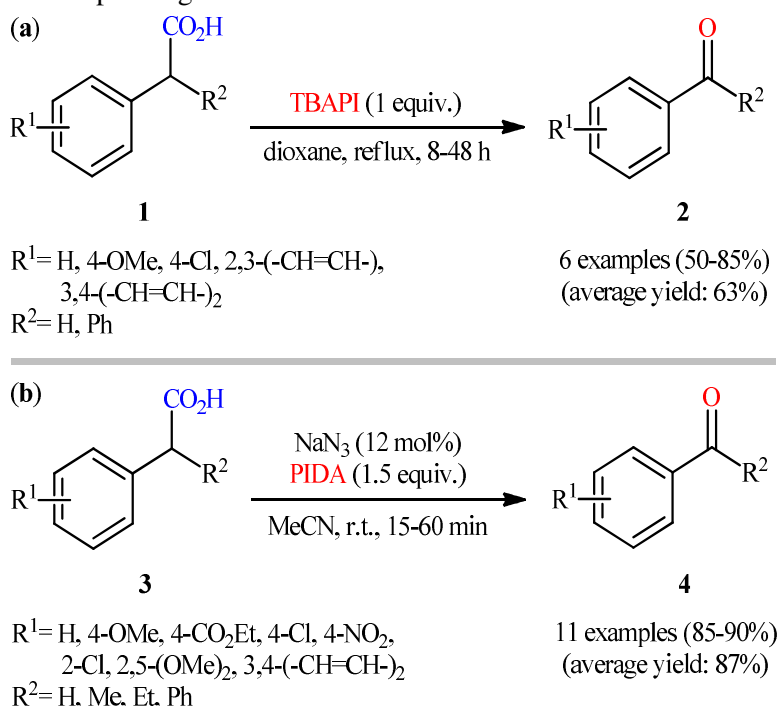
Scheme 2. (a) Metal-free oxidative decarboxylation of arylacetic acids 1 developed by Santaniello's group; (b) NaN$_3$-catalyzed oxidative decarboxylation of arylacetic acids 3 reported by Telvekar and Sasane.
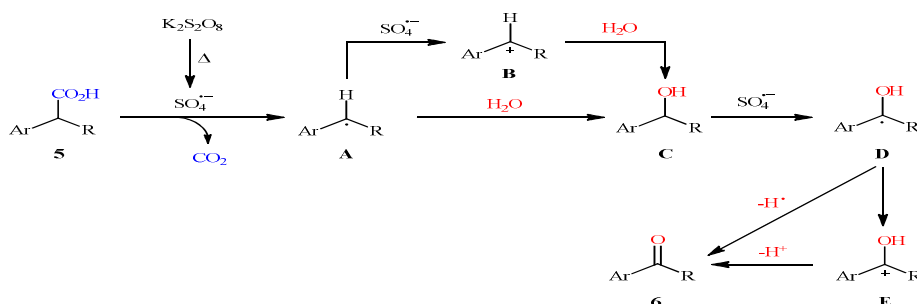
Following these works, Bhat and colleagues reported that easily available low-cost potassium persulfate (K$_2$S$_2$O$_8$) could act as efficient oxidant for oxidative decarboxylation of arylacetic acids under catalyst-free conditions [11]. Among the various common solvents like H$_2$O, MeCN, MeOH, DCE; the most environmentally benign solvent, water was found to be the most efficient for this conversion. Thus, in the presence of 2.0 equiv. of K$_2$S$_2$O$_8$ in H$_2$O under open air, a library of (hetero)arylacetic acids 5 bearing various functional groups smoothly underwent oxidative decarboxylation to give the corresponding aldehydes and ketones 6 in good to excellent yields (Scheme 3). Of note, replacing K$_2$S$_2$O$_8$ with some other oxidants (e.g., PIDA, PIFA, oxone) and performing the process under oxygen atmosphere in place of open air led to lower yields. No desired product was obtained in the lack of oxidant. Noteworthy, the authors demonstrated the scalability of the reaction since benzaldehyde and benzophenone could be obtained on a gram scale in high yield of 83% and 93%, respectively. Based on several control experiments, such as isotope labeling and radical trapping experiments, the authors suggested a plausible mechanistic pathway for this transformation, such as that shown in Scheme 4.

Scheme 3. $K_2S_2O_8$-mediated oxidative decarboxylation of (hetero)arylacetic acids **5**.
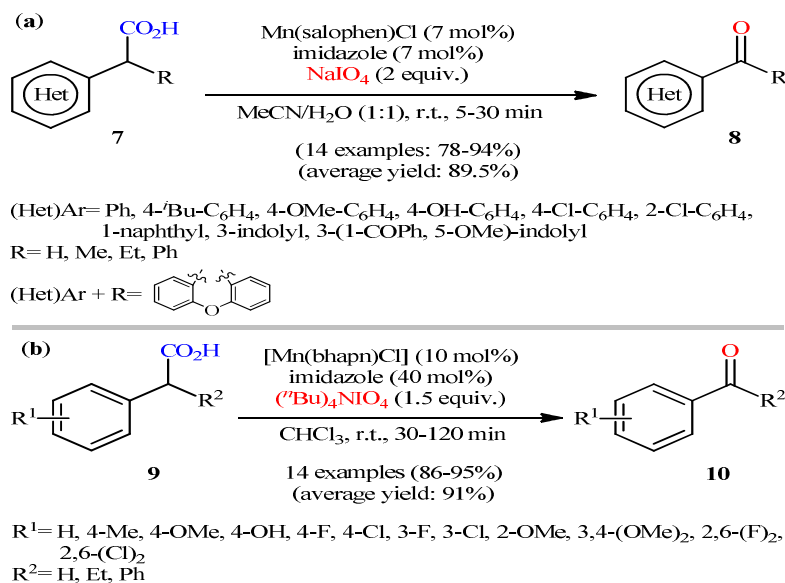

**Scheme 4.** Plausible mechanism for the formation of (hetero)aryl aldehydes and ketones 6.

3. Metal-catalyzed reactions

After pioneering work by Hirobe and his research group on iron-catalyzed oxidative decarboxylation of phenylacetic acids using the combination of iron tetraphenylporphyrin and iodosylbenzene as the catalytic system [12], the first general report of the synthesis of carbonyl compounds through the metal-catalyzed oxidative decarboxylation of respective phenylacetic acids was published in 2004 by Mirkhani *et al* [13]. In this study, they prepared a series of transition metal Schiff base complexes of the type M-salophen/BPB [(M= Fe, Mn, Co and Ni), BPB= *N,N'*-bis(2 pyridinecarboxamide)-1,2-benzene)] and investigated their potency as catalysts in oxidative decarboxylation of diphenylaceticacid using sodium periodate (NaIO$_4$) as the oxidant in the presence of different axial ligands (e.g., imidazole, 1-methylimidazole, 4-*t*-buthylpyridine, 4-methylpyridine, 2-methylpyridine, pyridine). The best conversion efficiency was obtained for the reaction performed in the presence of Mn-salophen as the catalyst and imidazole as the ligand. Under optimized conditions

various (hetero)arylacetic acids 7 underwent oxidative decarboxylation to form the corresponding carbonyl compounds 8 in good to excellent yields within 5-30 min (Scheme 5a). Beside arylacetic acids, α-hydroxyphenylacetic acids were also found to be compatible with this conversion. However, only a single example of such a reaction was reported in this study. Unfortunately, no aliphatic carboxylic acid was examined in this synthetic strategy. Five years later, the same authors improved the efficiency of this reaction in the term of yield by performing the process in the presence of manganese(III) tetra(4-pyridyl)porphyrin supported on cross-linked chloromethylated polystyrene, [Mn(T4PyP)-CMP] [14]. In a related investigation, Nasr-Esfahani and co-workers disclosed that various aromatic aldehydes and ketones 10 were formed in excellent yields from the corresponding arylacetic acids 9 employing [Mn(bhapn)Cl] as the catalyst and (^{n}Bu)$_4$NIO$_4$ as an oxidant (Scheme 5b) [15]. Based on literature, a likely catalytic cycle was proposed for this transformation, as depicted in Scheme 6.

(a)

Mn(salophen)Cl (7 mol%)
imidazole (7 mol%)
NaIO$_4$ (2 equiv.)

MeCN/H$_2$O (1:1), r.t., 5-30 min

(14 examples: 78-94%)
(average yield: 89.5%)

(Het)Ar= Ph, 4-^{t}Bu-C$_6$H$_4$, 4-OMe-C$_6$H$_4$, 4-OH-C$_6$H$_4$, 4-Cl-C$_6$H$_4$, 2-Cl-C$_6$H$_4$,
1-naphthyl, 3-indolyl, 3-(1-COPh, 5-OMe)-indolyl
R= H, Me, Et, Ph

(Het)Ar + R=

(b)

[Mn(bhapn)Cl] (10 mol%)
imidazole (40 mol%)
(^{n}Bu)$_4$NIO$_4$ (1.5 equiv.)

CHCl$_3$, r.t., 30-120 min

14 examples (86-95%)
(average yield: 91%)

R^1= H, 4-Me, 4-OMe, 4-OH, 4-F, 4-Cl, 3-F, 3-Cl, 2-OMe, 3,4-(OMe)$_2$, 2,6-(F)$_2$,
2,6-(Cl)$_2$
R^2= H, Et, Ph

Scheme 5. (a) Mn-catalyzed oxidative decarboxylation of (hetero)arylacetic acids 7 developed by Mirkhani; (b) Nasr-Esfahani's synthesis of carbonyl compounds 10.
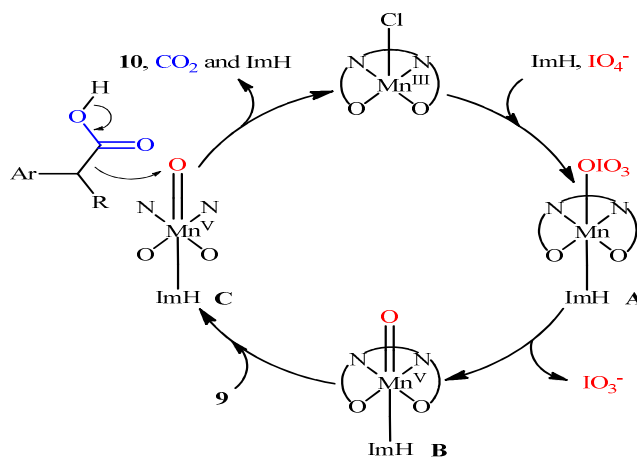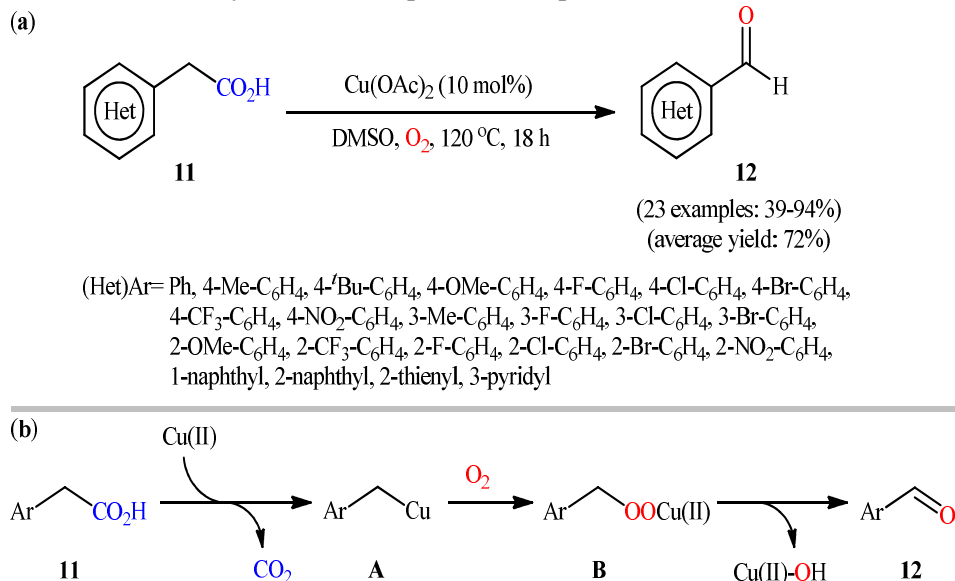

Scheme 6. Proposed mechanism for the reaction in Scheme 5b.

Consequently, with the aim of designing a greener procedure to (hetero)aromatic aldehydes through the metal-catalyzed oxidative decarboxylation of the respective (hetero)arylacetic acids, Feng and Song were able to demonstrate that a panel of 23 benzaldehyde derivatives 12 could be obtained in fair to almost quantitative yields from the corresponding arylacetic acids 11 using easily available, inexpensive Cu(OAc)$_2$ as the catalyst and molecular oxygen as the sole terminal oxidant (Scheme 7a) [16]. Although the reactions were done under ligand-free conditions without consuming any additive and oxidizing agent, requirement for drastic conditions of temperature may limit the utility of this method. Intriguingly, α-hydroxyphenylacetic acids were also worked well under standard conditions and gave the corresponding aldehydes in moderate to good yields. It should be mentioned that a series of α-alkyl-substituted phenylacetic acids [e.g., 2-cyclopentyl-2-phenylacetic acid, 2-(3-chlorophenyl)-3-methylbutanoic acid, 2-(4-isobutylphenyl)propanoic acid] were also subjected to the reaction but, unfortunately, they were sluggish to participate in this protocol and afforded poor yields or even no desired product at all. According to the authors proposed mechanism (Scheme 7b), the reaction proceeds through the decarboxylation of phenylacetic acid 11 with copper to from the active copper species A, followed by oxidation with O$_2$ into corresponding aldehyde 12 *via* the peroxy cuprate intermediate B. Shortly afterwards, Gould and colleagues revealed that oxidation of phenylacetic acids to benzaldehydes is possible in water using only copper(II) chloride as the oxidant [17]. However, in this preliminary work, only
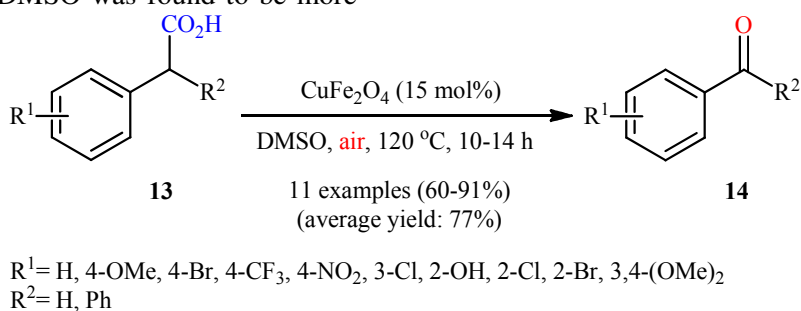
one example was provided, without any substrate scope   exploration.

(**a**)

11 → **12**

(23 examples: 39-94%)
(average yield: 72%)

(Het)Ar= Ph, 4-Me-C_6H_4, 4-^tBu-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4,
4-CF_3-C_6H_4, 4-NO_2-C_6H_4, 3-Me-C_6H_4, 3-F-C_6H_4, 3-Cl-C_6H_4, 3-Br-C_6H_4,
2-OMe-C_6H_4, 2-CF_3-C_6H_4, 2-F-C_6H_4, 2-Cl-C_6H_4, 2-Br-C_6H_4, 2-NO_2-C_6H_4,
1-naphthyl, 2-naphthyl, 2-thienyl, 3-pyridyl

(**b**)

11 CO_2 **A**   **B**   Cu(II)-OH   **12**

Scheme 7. (a) Cu-catalyzed oxidative decarboxylation of (hetero)arylacetic acids 11 under O_2 atmosphere; (b) Mechanistic proposal for the formation of benzaldehydes 12.

Recently, a related Cu-catalyzed oxidative decarboxylation of (hetero)arylacetic acids was reported by Rahman and co-workers [18]. They showed that in the presence of 15 mol% of magnetically recoverable and low cost spinel $CuFe_2O_4$ nanoparticles as the catalyst, oxidative decarboxylation of a library of arylacetic acids 13 under the open air, the most economic green oxidant, furnished the corresponding aromatic aldehydes and ketones 14 in good to excellent yields, ranging from 60% to 91% (Scheme 8). Notably, the outcome of the reaction was strongly dependent on solvent and temperature. DMSO was found to be more effective than other solvents, such as DMF, and H_2O and MeCN proved to be completely ineffective. The optimum temperature for this reaction was found to be 120 °C. Either increasing or decreasing the temperature led to decreased efficiency. It is notable that the catalyst could be easily separated from the final reaction mixture by means of an external magnet and reused for five consecutive runs, with only negligible loss of activity. The authors proposed mechanism for this transformation is analogous to the one depicted for in Scheme 7b.

13   11 examples (60-91%)   **14**
(average yield: 77%)

R^1= H, 4-OMe, 4-Br, 4-CF_3, 4-NO_2, 3-Cl, 2-OH, 2-Cl, 2-Br, 3,4-(OMe)$_2$
R^2= H, Ph

Scheme 8. $CuFe_2O_4$-catalyzed oxidative decarboxylation of (hetero)arylacetic acids 13 employing air as the oxidant.
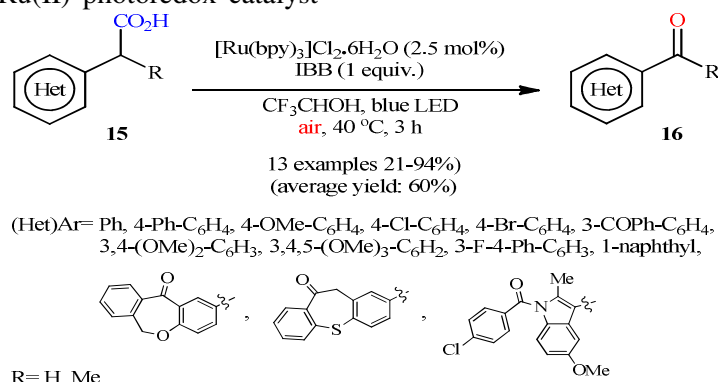
4. Photoredox-catalyzed reactions

In 2018, Murakami, Itami, and co-workers communicated the first example of aryl aldehydes/ketones synthesis through the decarboxylative oxidation of corresponding arylacetic acids under photoredox-catalyzed conditions [19]. By employing biphenylylacetic acid (felbinac; an anti-inflammatory drug) as the model reactant, the reaction variables such as photoredox catalysts and additives were carefully screened. The results proved that the combination of [Ru(bpy)$_3$]Cl$_2$·6H$_2$O, and hypervalent iodine 1-butoxy 1-λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (IBB) was the most suitable catalytic system and CF_3CH_2OH ideal solvent for this transformation. With these optimized reaction conditions, a panel of 13 (hetero)aryl aldehydes/ketones 16 were obtained in

relatively poor to excellent yields from the respective arylacetic acids 15 (Scheme 9). Synthetic utility of this methodology has been highlighted by accomplishing the transformation of various pharmaceuticals with functionalized arylacetic acid scaffolds (*e.g.*, flubiprofen, isoxepac, zaltoprofen, ketoprofen, and indomethacin). Unfortunately, no cyclization occurred when thienyl-, alkenyl-, or alkynylacetic acids were used as the substrates. In Scheme 10 a plausible mechanism for this transformation is outlined. In the beginning, the ground state Ru(II) photoredox catalyst

undergoes excitation by irradiation with blue light to produce the excited state * Ru(II), which reduces activated intermediate A (generated *via* the reaction of arylacetic acid 15 with IBB) to give carboxylic radical B and carboxylate C. Next, radical B undergoes decarboxylation to give benzyl radical D that, after quenching by O_2 produces intermediate E. Finally, disproportionation of intermediate E provides the observed products 16.

Scheme 9. photoredox-catalyzed decarboxylative oxidation of corresponding (hetero)arylacetic acids 15 developed by Murakami and Itami.
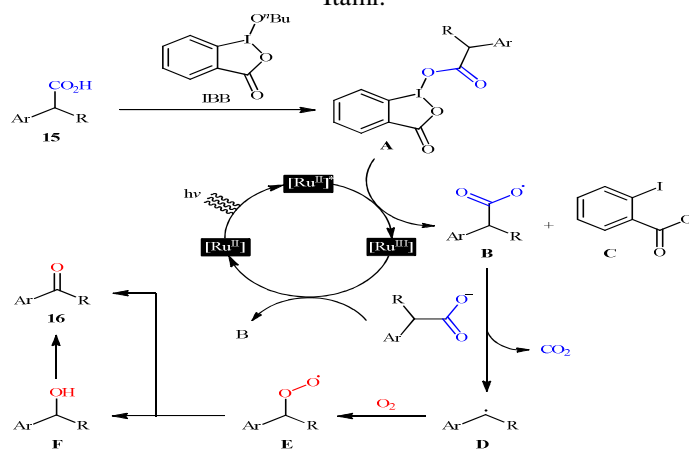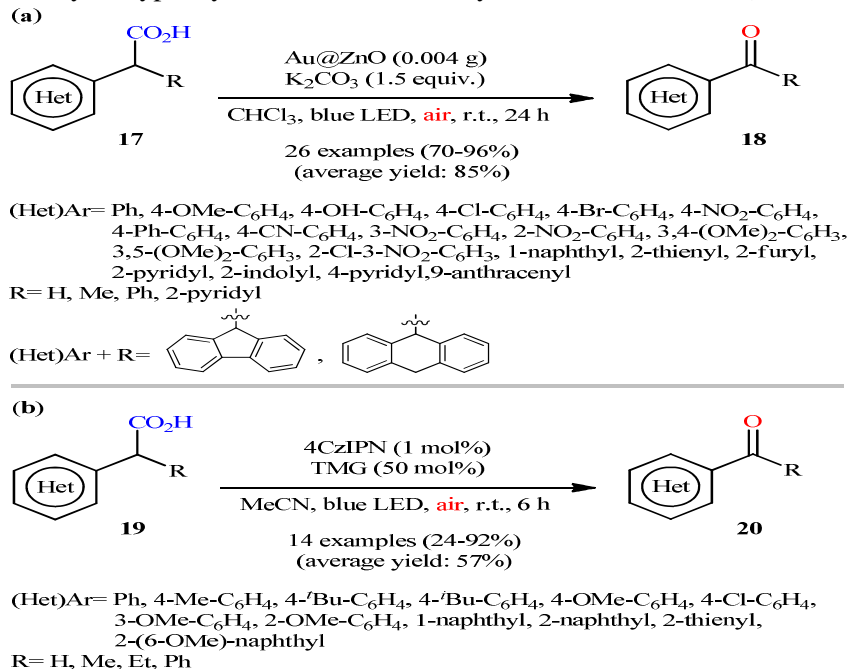

Scheme 10. Mechanistic explanation for the reaction in Scheme 9.

Subsequently, Bazyar and Hosseini-Sarvari reported the use of Au@ZnO core−shell nanoparticles in combination with K_2CO_3 for oxidative decarboxylation of a diverse range of functionalized (hetero)arylacetic acids 17 under the irradiation of blue LEDs [20]. The reactions were implemented under open air at room temperature and afforded the target (hetero)aryl aldehydes/ketones 18 in good to almost quantitative yields (Scheme 11a). Except (hetero)arylacetic acids, alkenylacetic acids could also be tolerated under the optimized conditions. Besides, two α-alkoxy-substituted acetic acids were also tested and gave the corresponding

ester derivatives. Interestingly, when the reactions were carried out under an inert atmosphere instead of air, instead of carbonyl compounds, corresponding decarboxylated products were obtained in moderate to excellent yields as the sole products. Concurrently, in a related investigation, the Chen-Yu group has identified 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as an efficient metal-free photoredox catalyst for oxidative decarboxylation of arylacetic acids under aerobic conditions (Scheme 11b) [21]. In this report, fourteen (hetero)aryl aldehydes/ketones 20 were synthesized in fair to excellent yields (24-92%) by means of only 1 mol% of 4CzIPN and 50 mol% of

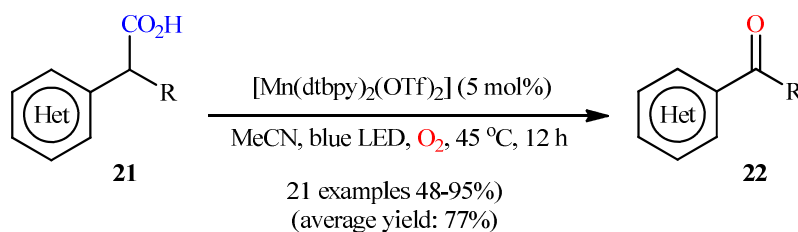1,1,3,3-tetramethylguanidine (TMG) in MeCN at room temperature under the irradiation of 25 W blue LEDs. Beside arylacetic acids, α-hydroxyphenylacetic acids were also well tolerated by this reaction. The process could also be easily conducted on a gram scale (84% yield on 10 mmol scale).

(a)

Au@ZnO (0.004 g)
K_2CO_3 (1.5 equiv.)
⟶
$CHCl_3$, blue LED, air, r.t., 24 h

17 **18**

26 examples (70-96%)
(average yield: 85%)

(Het)Ar= Ph, 4-OMe-C_6H_4, 4-OH-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-NO_2-C_6H_4,
4-Ph-C_6H_4, 4-CN-C_6H_4, 3-NO_2-C_6H_4, 2-NO_2-C_6H_4, 3,4-(OMe)$_2$-C_6H_3,
3,5-(OMe)$_2$-C_6H_3, 2-Cl-3-NO_2-C_6H_3, 1-naphthyl, 2-thienyl, 2-furyl,
2-pyridyl, 2-indolyl, 4-pyridyl,9-anthracenyl
R= H, Me, Ph, 2-pyridyl

(Het)Ar + R=

(b)

4CzIPN (1 mol%)
TMG (50 mol%)
⟶
MeCN, blue LED, air, r.t., 6 h

19 **20**

14 examples (24-92%)
(average yield: 57%)

(Het)Ar= Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-Cl-C_6H_4,
3-OMe-C_6H_4, 2-OMe-C_6H_4, 1-naphthyl, 2-naphthyl, 2-thienyl,
2-(6-OMe)-naphthyl
R= H, Me, Et, Ph

Scheme 11. (a) Au@ZnO-catalyzed oxidative decarboxylation of (hetero)arylacetic acids 17 under the irradiation of blue LEDs; (b) Visible-light-promoted oxidative decarboxylation of (hetero)arylacetic acids 19 catalyzed by 4CzIPN.
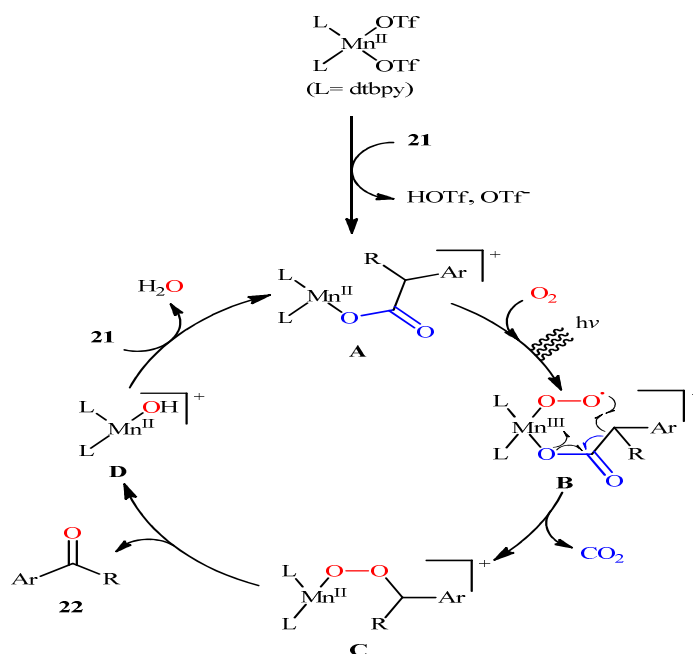
Very recently, Huang, Xiao, and co-workers disclosed the usefulness of non-heme Mn(II) catalysts for decarboxylative oxidation of arylacetic acid derivatives under ligand- and additive-free conditions [22]. Thus, in the presence of 5 mol% of [Mn(dtbpy)$_2$(OTf)$_2$] (dtbpy= 4,4-di-*tert*-butyl-2,2-dipyridyl)complex under oxygen atmosphere and blue light irradiation, decarboxylative oxidation of various (hetero)arylacetic acids 21 furnished the corresponding (hetero)aryl aldehydes/ketones 22 in moderate to quantitative yields, ranging from 48% to 95% (Scheme 12). Various important functional groups (e.g., OMe, F, Cl, Br, CF_3, NO_2) in the phenyl ring periphery of phenylacetic acids were well tolerated by this reaction, thus indicating its broad applicability. Importantly, apart from arylacetic acids and heteroarylacetic acids, alkyl arylacetic acids were also compatible with this scenario.

Of note, this methodology was also successfully applied in the synthesis of amides and carbamates from α-NHR-substituted acetic acids. The authors proposed a plausible mechanistic pathway for the formation of(hetero)aryl aldehydes/ketones 22, such as that shown in Scheme 13. Initially, (hetero)arylacetic acids 21 reacts with the Mn(II) precatalyst to form cationic intermediate A, which is subsequently oxidized by O_2 under visible light irradiation to afford superoxide radical B. This unstable intermediate attacks the benzylic carbon of the coordinated acid driven by the release of CO_2, resulting in the formation of the Mn(II)-peroxide C. Finally, decomposition of the unstable species C produces the target carbonyl product 22 and a Mn(II)-OH species D, which reacts with phenylacetic acid, regenerating intermediate A.

Scheme 12. Photo-Mn enabled oxidative decarboxylation of (hetero)arylacetic acids 21.

Scheme 13. Mechanism that accounts for the formation of (hetero)aryl aldehydes/ketones 22.

5. Conclusion

In this review, recent developments and also pioneering efforts on the direct one-pot synthesis of aldehydes and ketones *via* oxidative decarboxylation of easily available acetic acid derivatives have been discussed. It is shown that various aromatic, heteroaromatic, as well as aliphatic aldehydes/ketones are readily accessible by using this approach in a straightforward modular way. We hope that this review will be helpful to synthetic chemists in designing and synthesizing bioactive and natural carbonyl compounds through oxidative decarboxylation strategies.

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