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SHORT COMMUNICATION

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Copper-Catalyzed Decarboxylative Methylation of Aromatic Carboxylic Acids with $PhI(OAc)_2$

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Keywords: Synthetic methods / Decarboxylation / Methylation / Carboxylic acids / Copper / Radicals

The copper-catalyzed decarboxylative methylation of aromatic carboxylic acids was developed by using $PhI(OAc)_2$ to provide a new strategy for the methylation of aryl acids through the decarboxylation of alkyl acids. The mechanism and the roles of each reactant in the reaction were investigated extensively.

Introduction

Over the past few years, the decarboxylative transformation of carboxylic acids has gained extensive attention, and a rapidly growing number of reactions of this type have been reported.[1] As chemical reactants, carboxylic acids have many desirable properties and great advantages, which include low cost, nontoxicity, relatively high stability, and ready availability. Furthermore, as CO_2 is the sole by-product from carboxylic acids, decarboxylation reactions may reduce the formation of chemical wastes.[2] Most of the recently reported decarboxylative transformations involve transition-metal-catalyzed decarboxylative cross-coupling reactions of aromatic carboxylic acids. In transition-metal-catalyzed reactions, carboxylic acids may serve as synthetic equivalents of (pseudo)halides or organometallic reagents,[1c] and they undergo a variety of cross-coupling reactions.[3] In this context, most of the reactions involve carbon–carbon bond formation, and carbon–heteroatom forming reactions are quite rare.[4] However, decarboxylative reactions of aliphatic carboxylic acids have also attracted considerable interest, and quite a few novel reactions have been discovered.[5] Mechanistically, the decarboxylation of aromatic acids often involves the formation of organometallic species enabled by transition metals,[6] whereas aliphatic carboxylic acids decarboxylate through radical mechanisms or under oxidative conditions.[1a]

As one of the most common functional groups, the ester functionality is ubiquitous in organic molecules.[7] Conventional methods for the preparation of esters primarily involve esterification with acids and alcohols or transesterification with esters and alcohols.[8] As these two reactions are equilibrium reactions, an excess amount of one of the reagents has to be used or the water or alcohol product must be removed to force the reaction forward to the side of the product. The addition of dehydration reagents is an alternative efficient method, but this increases the complexity of the reaction system and produces a large amount of byproducts.[9] Owing to the importance of esters and the existing drawbacks of the current reactions, esterification is still the subject of extensive study, and a variety of new reactions have been disclosed,[10] which include a few novel transition-metal-catalyzed esterification reactions.[11] With the great advantages of carboxylic acids taken into consideration, decarboxylative esterification should be a novel intriguing reaction for the preparation of esters. However, this reaction is expected to be a challenge, because one of the carboxylic acids must undergo decarboxylation selectively. As mentioned previously, aliphatic carboxylic acids generally decarboxylate through a mechanism different to that of aromatic carboxylic acids, and this would provide the opportunity to achieve selective decarboxylation of either the aryl acids or the alkyl acids (Figure 1). On the basis of this reasoning, we envisioned that aryl acids could be esterified by decarboxylation of alkyl acids, which can decarboxylate through a radical mechanism to produce alkyl radicals. It is noted that esterification products arising from decarboxylation of aliphatic carboxylic acids, primar-

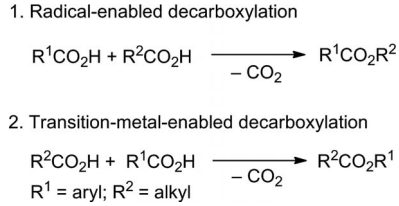

Figure 1. A new strategy for the synthesis of esters through the decarboxylation of carboxylic acids.

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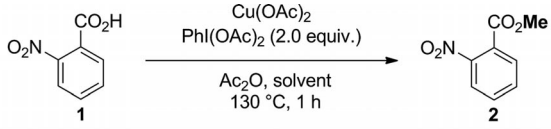
ily as lead tetracarboxylates, has been observed.[12] In these reactions, the esters were generally formed as coproducts, and the alkyl and carboxylate moieties are from the same alkyl acid. One exception is the allylation reaction of acids with lead tetraallylate.[13] Herein, we describe a novel decarboxylative methylation of aromatic carboxylic acids.

Results and Discussion

The research was initiated by the observation that methyl 2-nitrobenzoate was formed in 32% yield if 2-nitrobenzoic acid was treated with $PhI(OAc)_2$ and a catalytic amount of $Cu(OAc)_2$ in DMF (Table 1). Solvent screening revealed that the reaction gave a similar result with CH_3CN as the solvent and also that the methylation product was not produced in THF. Gratifyingly, the addition of acetic anhydride (1 equiv.) improved the yield to 88%. The yield almost remained unaffected if 0.5 equiv. acetic anhydride was used, but it decreased substantially in the case of 0.2 equiv. acetic anhydride. The yield was further improved to 94% by using a DMF/CH_3CN mixture as the solvent. With a satisfactory yield in hand, we investigated the effects of the reaction conditions on the yield. Therefore, the use of 0.15 equiv. $Cu(OAc)_2$ afforded a similar yield, but the yield decreased to 86% with the use of 0.1 equiv. catalyst. The use of 1 equiv. $PhI(OAc)_2$ resulted in a huge decrease in the yield, and lowering the temperature or shortening the reaction time also decreased the yield substantially. Furthermore, no methylation products were observed in the absence of $Cu(OAc)_2$ or $PhI(OAc)_2$.

Having identified the optimal protocol for the methylation of 2-nitrobenzoci acid, we probed the substrate scope with regard to the aromatic carboxylic acids. The protocol proved to be compatible with a broad range of benzoic acids and tolerated a wide variety of functional groups. As summarized in Table 2, both *meta*- and *para*-nitrobenzoic acids underwent the methylation reaction effectively, albeit in a lower yield. A range of electron-withdrawing groups were well tolerated, including nitrile, trifluoromethyl,

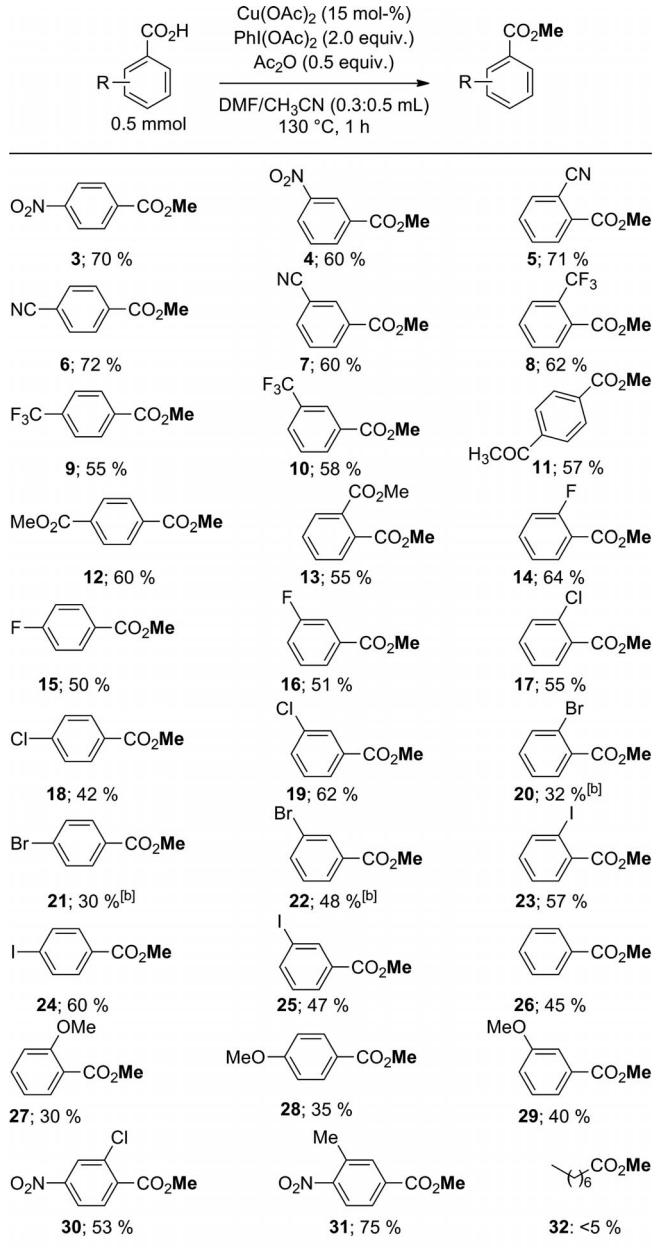
Table 1. Survey of the reaction conditions.



Entry	$Cu(OAc)_2$ [equiv.]	Ac_2O [equiv.]	Solvent (mL)	Yield [%][a]
1	0.2	0	DMF (0.5)	32
2	0.2	0	MeCN (0.5)	30
3	0.2	0	THF (0.5)	0
4	0.2	1	DMF (0.5)	88
5	0.2	0.5	DMF (0.5)	86
6	0.2	0.2	DMF (0.5)	41
7	0.2	0.5	DMF/CH_3CN (0.3:0.5)	94
8	0.15	0.5	DMF/CH_3CN (0.3:0.5)	94 (88[b])
9	0.1	0.5	DMF/CH_3CN (0.3:0.5)	86
10[c]	0.15	0.5	DMF/CH_3CN (0.3:0.5)	47
11[d]	0.15	0.5	DMF/CH_3CN (0.3:0.5)	67
12[e]	0.15	0.5	DMF/CH_3CN (0.3:0.5)	73
13[f]	0	0.5	DMF/CH_3CN (0.3:0.5)	0
14[g]	0.15	0.5	DMF/CH_3CN (0.3:0.5)	0

[a] Determined by analysis of the crude product by ^1H NMR spectroscopy by using $CHCl_2CHCl_2$ as an internal standard. [b] Yield of the isolated product. [c] $PhI(OAc)_2$ (1 equiv.). [d] 110 °C. [e] 10 min. [f] No $Cu(OAc)_2$. [g] No $PhI(OAc)_2$.

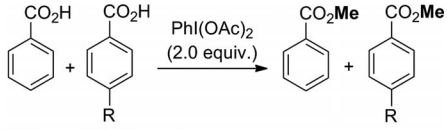
Table 2. Substrate scope of the methylation of aromatic carboxylic acids.[a]



[a] Yield of the isolated product. [b] Determined by ^1H NMR spectroscopy.

ketone, and ester. Substrates with fluoride, chloride, and iodide at the *ortho*, *meta*, and *para* positions were methylated under the reaction conditions. The methylation of benzoic acid and its analogues with methoxy groups gave lower yields, and disubstituted benzoic acids were also compatible. No significant amount of the methylation product for octanoic acid was observed.

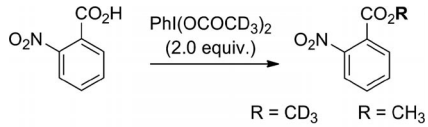
Generally, electron-poor benzoic acids were methylated in higher yields than the electron-rich ones. To further study the relative reactivities of different benzoic acids, we performed the reactions by using equal amounts of benzoic acid and a substituted benzoic acid. As shown in Figure 2, the experiments revealed that benzoic acid was methylated far less effectively than benzoic acids with electron-withdrawing groups (NO_2 and CN) and slightly more efficiently than benzoic acids with electron-donating groups (OAc and OMe).



R = NO_2	32 %	86 %
R = CN	23 %	70 %
R = OAc	30 %	27 %
R = OMe	26 %	18 %

Figure 2. Comparison of the reactivities of benzoic acid and substituted benzoic acids. Conditions: $Cu(OAc)_2$ (15 mol-%), Ac_2O (0.5 equiv.), DMF/CH_3CN (0.3:0.5 mL), 130 °C, 1 h.

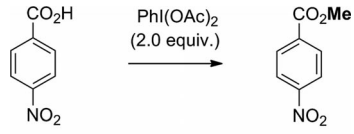
Mechanistic experiments were conducted to gain insight into the mechanism of the methylation reaction. First, to investigate the source of the methyl group, we performed the methylation reaction by using $PhI(OCOCD_3)_2$ and $Cu(OTf)_2$ (Tf = trifluoromethylsulfonyl) in lieu of $PhI(OAc)_2$ and $Cu(OAc)_2$ respectively. As shown in Figure 3, in the absence of acetic anhydride, [D_3]methyl 2-nitrobenzoate was almost the sole product. Both methylated and [D_3]-methylated products were formed in the presence of acetic anhydride. These results demonstrated that the sources of the methyl group were $PhI(OAc)_2$ and acetic anhydride, and $PhI(OAc)_2$ should be the initial source. To obtain some more information about the role of acetic anhydride, we performed several comparison experiments (Figure 4). Therefore, acetic anhydride was replaced with propionic anhydride. The yield decreased to 40%, which was close to



	R = CD_3	R = CH_3
No Ac_2O	16%	1%
Ac_2O (1 equiv.)	47%	26 %
Ac_2O (0.25 equiv.)	16 %	3 %

Figure 3. Investigation into the source of the methyl group. Conditions: $Cu(OTf)_2$ (15 mol-%), DMF/CH_3CN (0.3:0.5 mL), 130 °C, 1 h.

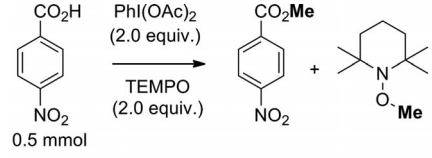
the yield of the reaction in the absence of any hydrides. Furthermore, the addition of acetic acid (1 equiv.) resulted in an even lower yield. On the basis of these observations and the previous report on the role of anhydrides in the decomposition of $PhI(OAc)_2$, acetic anhydride may promote the methylation reaction by acetylating any diacetate that may be hydrolyzed by trace amounts of water.[14]



No additives	36 %
$(CH_3CH_2CO)_2O$ (0.5 equiv.)	40 %
CH_3COOH (1.0 equiv.)	20 %

Figure 4. Investigation into the role of acetic anhydride. Conditions: $Cu(OAc)_2$ (15 mol-%), DMF/CH_3CN (0.3:0.5 mL), 130 °C, 1 h.

Next, the radical inhibitor 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) was added into the reaction to investigate if a radical was involved in this methylation reaction. As shown in Figure 5, no methylated products were observed in the presence of TEMPO (2 equiv.), and more importantly, 24% *O*-methylated TEMPO was formed. This provided strong evidence that a radical mechanism was operative in this methylation reaction. Notably, a similar amount of *O*-methylated TEMPO was yielded even in the absence of $Cu(OAc)_2$, which implies that $Cu(OAc)_2$ was not involved in the formation of the methyl radical. Actually, aryl iodine diacetate has been reported to undergo thermal decomposition spontaneously to generate alkyl radicals via acetoxy radical intermediates [Figure 6, Eq. (1)].[15] It is noteworthy that the decomposition of aryl iodine diacetate might be an ion-pair process [Figure 6, Eq. (2)]. In this process, aryl acetate and MeI are produced.[14] The methylation product in this report could result from the reaction be-



No $Cu(OAc)_2$	0	24 % 0.24 mmol
$Cu(OAc)_2$ (15 mol-%)	0	20 % 0.20 mmol

Figure 5. Investigation into the generation of methyl radicals. Conditions: Ac_2O (0.5 equiv.), DMF/CH_3CN (0.3:0.5 mL), 130 °C, 1 h.

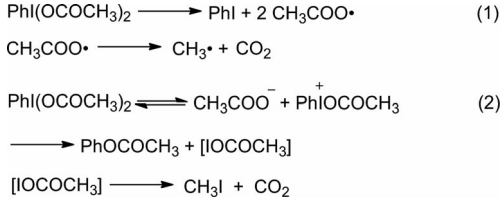
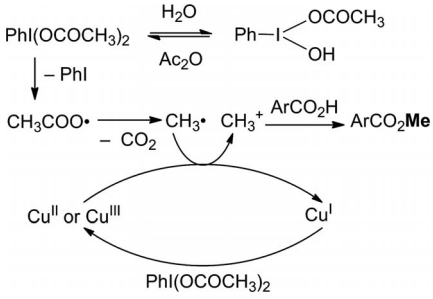


Figure 6. Possible pathways for the decarboxylation of $PhI(OAc)_2$.[14]

tween aryl acids and MeI. However, phenyl acetate was not observed, and almost 100% PhI was recovered, which was against a methyl iodide mechanism.

As the methylation products were not formed in the absence of a copper catalyst and $Cu(OAc)_2$ was not involved in the formation of the radical, the copper catalyst should be responsible for the methylation step. Noteworthy, it has been reported that Cu^{II} can oxidize alkyl radicals to alkyl esters with carboxylic acids. Therefore, we propose a radical mechanism for the methylation of aryl acids, as shown in Scheme 1. $PhI(OAc)_2$ decomposes to yield acetoxy radicals, which undergo decarboxylation to afford methyl radicals. The resulting methyl radicals are oxidized by Cu^{II} or Cu^{III} to form methylated aryl acids and generate Cu^{I} species, which is oxidized, very likely by $PhI(OAc)_2$, to Cu^{II} or Cu^{III} to continue the catalytic cycle.

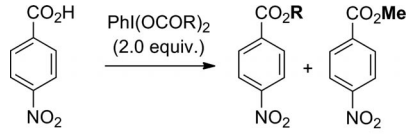


Scheme 1. Proposed mechanism for the decarboxylative methylation of aryl acids.

As with carbocations, the stability of radicals increases with additional alkyl substitution. In the decarboxylation of lead tetraacetate, the relative ease of decarboxylation of carboxylic acids is related to the stability of the carbon radicals resulting from the loss of carbon dioxide: tertiary > secondary > primary.[12a] Recently, the Liu and Zhu groups independently reported the decarboxylative alkylation of alkenes with aryl iodine diacetate.[16] In these radical-involved reactions, the reactivity of the carboxylic acids also paralleled the stability of the carbon radicals. As such, after establishing that a radical mechanism was operating in this methylation reaction, we envisioned that this protocol would be applicable to the alkylation of aryl acids with other alkylation reagents. Therefore, ethylation and *tert*-butylation reactions were conducted with $PhI(OCOEt)_2$ and $PhI(OCO\mathit{t}Bu)_2$. Unexpectedly, almost no desired products were observed no matter what anhydrides were used, that is, acetic anhydride or propionic/*tert*-butanoic anhydride (Figure 7). In the reactions with the use of acetic anhydride, methylation products were generated in low yields. The mechanism responsible for this outcome remains to be explored.

Conclusions

In summary, aliphatic and aromatic carboxylic acids may decarboxylate through different mechanisms. The decarboxylation of alkyl acids generally involves a radical process



R = Et	Ac_2O	2 %	12 %
	$(EtCO)_2O$	<1 %	–
R = *t*Bu	Ac_2O	n.d.	11 %
	$(\mathit{t}BuCO)_2O$	n.d.	–

Figure 7. Attempts at the ethylation/*tert*-butylation of aryl acids. Conditions: $Cu(OAc)_2$ (15 mol-%), Ac_2O (0.5 equiv.), DMF/CH_3CN (0.3:0.5 mL), 130 °C, 1 h.

that produces alkyl radicals, which provides an opportunity for the development of the decarboxylative alkylation of aromatic carboxylic acids. By taking advantage of this opportunity, we developed the Cu-catalyzed methylation of aromatic carboxylic acids with $PhI(OAc)_2$. The mechanism and the roles of each reagent in the reaction were investigated. This reaction demonstrated that aromatic carboxylic acids may be alkylated through the decarboxylation of alkyl acids, which would provide an advantageous method for the synthesis of esters. More detailed mechanistic studies and the exploration of other decarboxylative alkylation reactions in addition to the methylation reaction, especially for reactions in which simple alkyl acids are used, are underway in our laboratory.

Experimental Section

General Procedure for the Methylation of Aromatic Carboxylic Acids: A 50 mL sealed tube (with a Teflon high-pressure valve) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (13.6 mg, 0.075 mmol) followed by carboxylic acid (0.5 mmol), Ac_2O (23.3 μL, 0.25 mmol), $PhI(OAc)_2$ (322 mg, 1 mmol), DMF (0.3 mL), and MeCN (0.5 mL). After the reaction mixture was stirred at 130 °C for 1 h, it was cooled to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL, 2×). The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel preparative TLC to give the corresponding product.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data of synthesized compounds, and copies of the ^1H NMR and ^{13}C NMR spectra.

Acknowledgments

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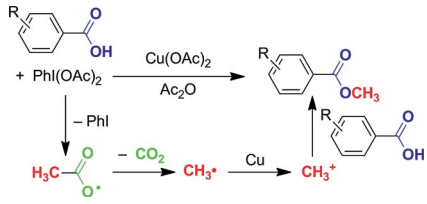
SHORT COMMUNICATION

Decarboxylation

The acetate of $PhI(OAc)_2$ can undergo decarboxylation selectively in the presence of aromatic carboxylic acids through a radical mechanism, and the resulting methyl radical may methylate a range of aryl acids with the aid of copper and acetic anhydride to afford methyl acetates. This novel reaction demonstrates a new esterification strategy through the decarboxylation of alkyl carboxylic acids.



Keywords: Synthetic methods / Decarboxylation / Methylation / Carboxylic acids / Copper / Radicals

