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Direct oxidative cyclization of 3-arylpropionic acids using PIFA or Oxone: synthesis of 3,4-dihydrocoumarins

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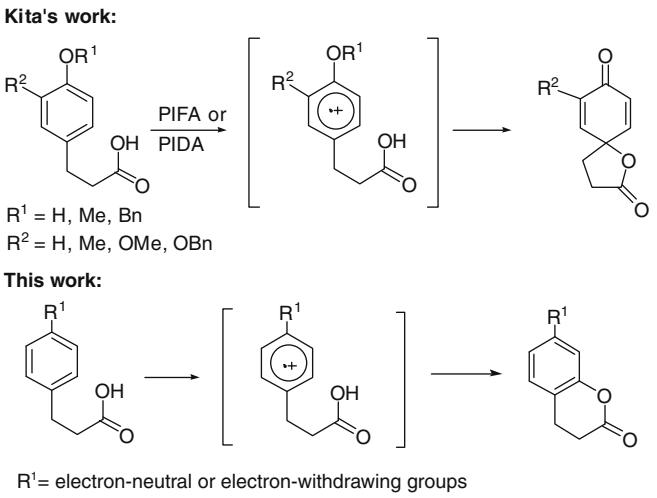
ABSTRACT

The direct oxidative cyclization of 3-arylpropionic acids using PIFA or Oxone is reported. In the presence of $BF_3{\cdot}OEt_2$, the reaction of 3-arylpropionic acids with PIFA or Oxone proceeded smoothly at 30 °C to give 3,4-dihydrocoumarins in good to excellent yields.

Coumarin and its derivatives are one of the most privileged structural motifs frequently found in natural products and pharmaceuticals.[1] As an important class of coumarins, 3,4-dihydrocoumarins are widely distributed in nature[2] and exhibit some interesting biological activities, such as anti-herpetic, anti-inflammatory, anti-oxidative, anti-aging, and anti-cancer activities.[3] Therefore, development of efficient methods for the synthesis of dihydrocoumarins have attracted great interest in recent years.[4] The conventional methods for the syntheses of dihydrocoumarins include (1) the transition-metal-catalyzed hydrogenation of coumarins;[5] (2) Lewis or protonic acid-mediated hydroarylation of cinnamic acids with phenols;[6] (3) the transition-metal-catalyzed intramolecular electrophilic hydroarylation of alkene substrates;[7] (4) Lewis acid-mediated reaction of highly activated phenols with acrylonitriles,[8] 5-alkylidene Meldrum's acids[9] and hydroxyketene-*S*,*S*-acetals;[10] (5) the Baeyer–Villiger oxidation of 1-indanones formed in situ by the Friedel–Crafts cyclization of 3-arylpropionic acids.[11] However, many of these methods suffer disadvantages from using a large excess of expensive transition-metals, such as $Pb(OAc)_2$,[7f–h] Ru(I),[4c] Ru(III),[7e] $Y(OTf)_3$,[6a] $Yb(OTf)_3$,[9] $Cr(CO)_5$,[4e] and harsh conditions. To achieve the environmental demands for 'green' chemical procedures, we were prompted to explore the feasibility of dihydrocoumarin synthesis by transition-metal-free oxidative C–O formation reaction from the corresponding carboxylic acids.

Recently, utilization of hypervalent iodine compounds in oxidative reactions has received great attention for their low toxicity compared with heavy metal oxidants, mild reaction conditions, special reactivity, and easy handling.[12] Several novel methods have been developed for the syntheses of lactones by intramolecular C–O bond formation using hypervalent iodine reagents.[13] Kita and co-workers reported the cyclization of *para*-substituted phenol[14] or phenol ether derivatives[15] to spiro dienone lactones using hypervalent iodine(III) reagents (Scheme 1). This method involves oxidation of phenols or phenol ethers to reactive electrophilic intermediates which are then trapped by carboxylic acid moiety. However, there is no report for the oxidative cyclization of electron-neutral or electron-deficient 3-arylylpropionic acids. We envisioned that oxidation of 3-arylylpropionic acids with hypervalent iodine reagents would generate radical cation intermediates, which could be attacked by carboxylic acid moiety to provide bicyclolactones. Herein, we disclose our investigation for the oxidative cyclization of 3-arylpropionic acids to 3,4-dihydrocoumarins using hypervalent iodine reagents as oxidants.

The initial attempts of the cyclization of 3-phenylpropionic acid (**1a**) with phenyliodine(III) diacetate (PIDA) or phenyliodine(III)



Scheme 1. Cyclization of *para*-substituted phenol or phenol ether derivatives.

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E-mail address: ygu01@ustc.edu.cn (Y. Gu).

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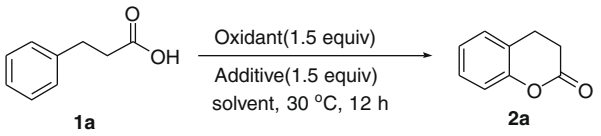
Table 1
Optimization of reaction conditions using PIDA or PIFA as an oxidant[a]



1a **2a**

Entry	Oxidant	Additive	Solvent	Yield[b] (%)
1	PIDA or PIFA	None	CH_2Cl_2	ND[c]
2	PIDA or PIFA	None	CH_3CN	ND
3	PIDA or PIFA	None	AcOH	ND
4	PIDA or PIFA	None	CF_3CH_2OH	<5
5	PIFA	None	TFA	17
6	PIDA	None	TFA	<5
7	PIFA	$BF_3{\cdot}OEt_2$	TFA	78
8	PIFA	$BF_3{\cdot}OEt_2$	TFA/CH_2Cl_2	62[d]

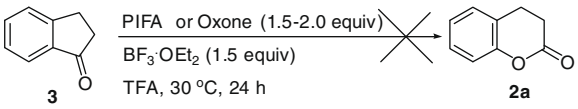
[a] Unless otherwise specified, all the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.3 mmol of oxidant, and 0.3 mmol of additive in 1 mL of solvent at 30 °C for 12 h.
[b] Isolated yield after column chromatography.
[c] No desired product was detected by TLC analysis.
[d] 0.2 mL of TFA and 1 mL of CH_2Cl_2 were used.

bis(trifluoroacetate) (PIFA) in CH_2Cl_2, CH_3CN and AcOH did not give any 3,4-dihydrocoumarin (**2a**) at all, and no conversion of **1a** was observed (Table 1, entries 1–3). When CF_3CH_2OH was used as a solvent, trace amount of **2a** was obtained under otherwise identical conditions (entry 4). To our pleasure, when TFA was employed as a solvent, cyclization of **1a** with PIFA provided the product **2a** in 17% yield (entry 5). While the analogous reaction gave only trace amount of **2a** with PIDA as an oxidant (entry 6). Notably, activation of PIFA with Lewis acid $BF_3{\cdot}OEt_2$ improved the reaction dramatically (entry 7).[16] In addition, when CH_2Cl_2 (5:1 CH_2Cl_2/TFA) was used as co-solvent, the reaction afforded the product **2a** in a slightly lower yield (entry 8). As a result, when the reaction was carried out in the presence of 1.5 equiv PIFA and 1.5 equiv $BF_3{\cdot}OEt_2$ in TFA at 30 °C, the best result was achieved.

With optimized conditions in hand, next we examined the reaction scope and the results are summarized in Table 2. This reaction was compatible with a variety of functionalities, including methyl, phenyl, fluoride, bromide, iodide, and ester groups. The reaction of 3-(4-methylphenyl)propionic acid (**1b**) with PIFA provided the cyclized product **2b** in 80% yield (entry 2). When the methyl group was introduced to the *ortho* position of phenyl ring, the reaction gave a slightly lower yield of **2c**, probably due to steric effect (entry 3). When the methyl group was introduced to the *meta* position of phenyl ring, two products **2da** and **2db** were obtained in 82% yield as a 2:1 mixture with a less sterically hindered product **2da** as the major (entry 4).[17] When the *para* position of phenyl ring was substituted with halogens (F, Br, I), the reaction generally proceeded well to give corresponding products **2e–g** in 54–79% yields (entries 5–7). It is noteworthy that when the substrate with an electron-withdrawing group, ester group at the *para* position of phenyl ring was employed, the reaction gave the cyclized product **2h** in a slightly lower yield for a longer reaction time (entry 8). Nevertheless, when the electron-donating group, methoxy group, was introduced to the *para* position of phenyl ring, the reaction failed to yield any desired product **2i**; instead, a complex mixture was obtained (entry 9).[18] To expand the substrate scope, we examined the substitution effect on the chain of 3-arylpropionic acid. It was found that when the substrates with methyl or phenyl group at the β-position of the carboxylic acid were employed, the reaction proceeded smoothly to give the products **2j** and **2k** in 90% and 75% yields, respectively (entries 10 and 11). Notably, when the substrate contains the hydroxyl group at the β-position of the carboxylic acid, the reaction gave the dehydrated product **2l** in moderate yield (entry 12).

To make this reaction more synthetically applicable, we extended our research to seek low-cost and 'greener' oxidants. Peroxides as inexpensive, environmentally benign oxidants are extensively used in modern organic synthesis. Due to their prominent properties, several peroxides were explored in the oxidative cyclization of 3-phenylpropionic acid (**1a**) (Table 3). It was found that peroxides, such as *m*-CPBA, H_2O_2, and *t*-BuOOH failed to provide any desired product **2a** in this reaction (entries 1–3). To our delight, both $K_2S_2O_8$ and Oxone were effective to this transformation. In the presence of 2.0 equiv oxidants and 1.5 equiv of $BF_3{\cdot}OEt_2$ in TFA at 30 °C, the reactions provided **2a** in 42% and 61% yields, respectively (entries 4 and 5). In addition, Lewis acid $BF_3{\cdot}OEt_2$ is also essential in this transformation (entries 5 and 6). This result indicated that $BF_3{\cdot}OEt_2$ probably activated the epoxide intermediate **8** formed in the reaction and facilitated this transformation (Scheme 2). Careful examination of the solvent showed TFA is the ideal solvent (entries 7–9). Therefore, using Oxone[19] as an oxidant and $BF_3{\cdot}OEt_2$ as an additive in TFA were chosen as desired reaction conditions.

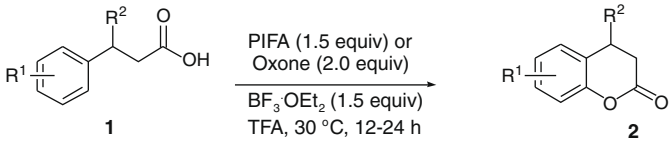
In the presence of 2.0 equiv Oxone and 1.5 equiv $BF_3{\cdot}OEt_2$, the reaction of acids **1a–l** in TFA proceeded smoothly to provide cyclized products **2a–l** in 16–71% yields (Table 2). This reaction proceeded generally comparable or moderately lower yields compared with PIFA-mediated reaction. This transformation could be applied to the substrates containing various functional groups, including methyl, phenyl, halides, and methoxy groups (entries 2–11). Notably, in some cases, Oxone showed the improved functional group tolerance relative to PIFA. For example, the cyclization of methyl ether **1i** provided 16% yield of **2i**, the analogous reaction failed to yield **2i** with PIFA as an oxidant (entry 9). However, when the substrate contains an electron-withdrawing group, (e.g., in 3-(4-carbomethoxyphenyl)propionic acid (**1h**)), the reaction was not successful (entry 8).



3 **2a** (1)

It should be noteworthy that the oxidation of 1-indanone (**3**) with PIFA or Oxone in the presence of $BF_3{\cdot}OEt_2$ in TFA did not provide 3,4-dihydrocoumarin (**2a**) (Eq. 1). Therefore, the formation of 1-indanone from the 3-phenylpropionic acid with TFA followed by the oxidation to dihydrocoumarin should be excluded. Two plausible path ways are proposed according to the literature examples and our above experimental results (Scheme 2).[15c,20] First, the one electron oxidation of aromatic ring of **1** by PIFA forms the radical cation **4**. Then intramolecular nucleophilic attack by the carboxylic acid moiety on radical cation yields the bicyclolactone cation **5** (path a) or spiro lactone cation **6** (path b); rearrangement of the carboxylic unit of **6** leads to intermediate **5**, the deprotonation of **5** generates dihydrocoumarin **2**. Additionally, the reaction of phenol derivatives (R^1 = OH) with PIFA and $BF_3{\cdot}OEt_2$ at −78 °C afforded the spiro dienone lactone **7** in 57% yield. This result suggests that the reaction may proceed via the rearrangement pathway. Furthermore, we also proposed the mechanism of the oxidative cyclization by Oxone.[21] Oxidation of **1** by Oxone forms the epoxide **8**, followed by intramolecular nucleophilic attack of epoxide with carboxylic acid moiety to provide the intermediate **9**. Last dehydration of **9** furnishes dihydrocoumarin **2**.

Table 2
Reaction of 3-arylpropionic acid with PIFA or Oxone[a]



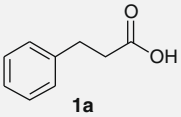
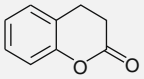
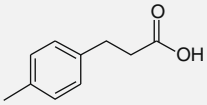
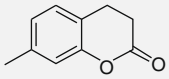
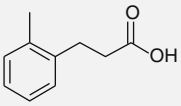
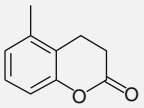
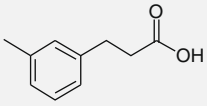
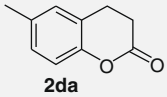
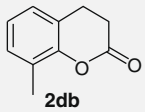
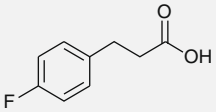
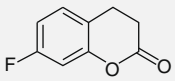
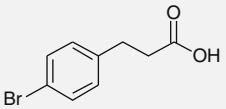
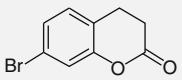
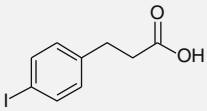
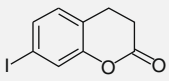
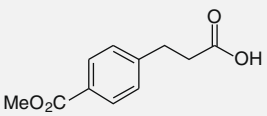
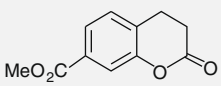
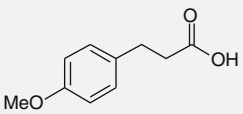
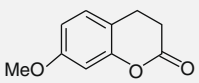
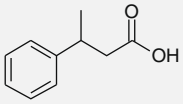
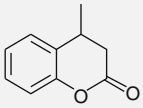
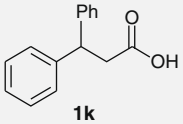
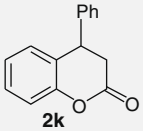
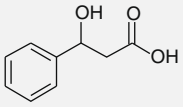
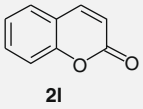
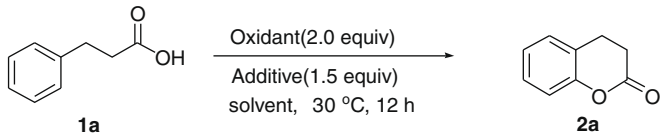
Entry	Substrate	Product	Time (h)	Yield[b] (%) PIFA/Oxone
1	 **1a**	 **2a**	12	78/61
2	 **1b**	 **2b**	12	80/61
3	 **1c**	 **2c**	16	63/44
4	 **1d**	 **2da**  **2db**	12	82/61(2:1)
5	 **1e**	 **2e**	16	54/49
6	 **1f**	 **2f**	12	79/58
7	 **1g**	 **2g**	12	65/56
8	 **1h**	 **2h**	24	50/ND[c]
9	 **1i**	 **2i**	12	ND/16

Table 2 (*continued*)

Entry	Substrate	Product	Time (h)	Yield[b] (%) PIFA/Oxone
10	 **1j**	 **2j**	12	90/71
11	 **1k**	 **2k**	12	75/66
12	 **1l**	 **2l**	16	48/51

[a] Reactions were carried out with 0.2 mmol of **1**, 0.3 mmol of PIFA or 0.4 mmol of Oxone, 0.3 mmol of $BF_3{\cdot}OEt_2$ in 1 mL of TFA at 30 °C.
[b] Isolated yield after column chromatography.
[c] No desired product was detected by TLC analysis.

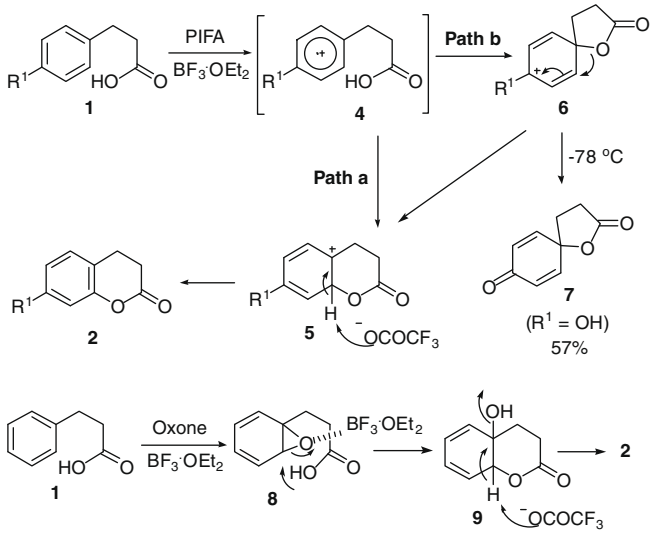
Table 3
Optimization of reaction conditions using peroxide as an oxidant[a]



1a **2a**

Entry	Oxidant	Additive	Solvent	Yield[b] (%)
1	*m*-CPBA	$BF_3{\cdot}OEt_2$	TFA	ND[c]
2	H_2O_2	$BF_3{\cdot}OEt_2$	TFA	ND
3	*t*-BuOOH	$BF_3{\cdot}OEt_2$	TFA	<5
4	$K_2S_2O_8$	$BF_3{\cdot}OEt_2$	TFA	42
5	Oxone	$BF_3{\cdot}OEt_2$	TFA	61
6	Oxone	None	TFA	35
7	Oxone	$BF_3{\cdot}OEt_2$	CH_2Cl_2	ND
8	Oxone	$BF_3{\cdot}OEt_2$	CF_3CH_2OH	ND
9	Oxone	$BF_3{\cdot}OEt_2$	AcOH	ND

[a] Unless otherwise specified, all the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.4 mmol of oxidant, and 0.3 mmol of additive in 1 mL of solvent at 30 °C for 12 h.



Scheme 2. Proposed mechanism of lactonization of 3-arylpropionic acid.

In conclusion, we developed a novel method for the synthesis of 3,4-dihydrocoumarin through direct oxidative cyclization of 3-arylpropionic acids using PIFA or Oxone as an oxidant. The synthetic utility of these reactions is enhanced by using Oxone as an inexpensive, safe, and environmentally benign oxidant. Ongoing work to expand the substrate scope and apply this reaction to the synthesis of more complex products is underway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.10.112.

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17. The ratio of products **2da** and **2db** was determined from the mixture of the products by ^{1}H NMR spectrum.
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