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Silver-catalyzed facile decarboxylation of coumarin-3-carboxylic acids

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ABSTRACT

A simple and highly efficient protocol with mild reaction conditions has been developed that allows the smooth protiodecarboxylation of diversely functionalized coumarin-3-carboxylic acids. In the presence of catalytic amounts of Ag_2CO_3 and acetic acid, even un-activated coumarin-3-carboxylic acids were converted in good to excellent yields and with great preparative ease to the corresponding coumarin derivatives.

1. Introduction

Carboxylate groups are frequently used as directing groups or templates in the synthesis of many organic molecules. In part, this is due to the possibility of removal via decarboxylation reactions.[1] Furthermore, decarboxylation of carboxylic acids is the key step in atom-economical oxidative couplings for the construction of C–C bonds.[2] Consequently, significant effort has been directed toward the protiodecarboxylation of aromatic and heteroaromatic carboxylic acids.

Earlier reports on the protiodecarboxylation of aromatic acids had limited practical applicability, involving harsh conditions and the use of stoichiometric amounts of copper or silver salts.[3,4] While mercury mediated protiodecarboxylations readily proceed under milder reaction conditions, their synthetic utility is restricted by the requirement for stoichiometric mercury salts and the involvement of toxic organomercury intermediates.[4,5] Recently, Gooßen et al.[6] disclosed protiodecarboxylation of arene carboxylic acids with catalytic amounts of copper/1,10-phenanthroline-complex, albeit the practical applicability of the scope was limited by it's requirement of high temperatures (160–190 °C). As investigations were directed toward decreasing the high temperature required in protiodecarboxylation reactions to decrease the thermal stress during the course of the reaction and expand substrate compatibility, Kozlowski et al.[7] presented palladium catalyzed protiodecarboxylation of particularly electron-rich bis-*ortho*-substituted aromatic carboxylic acids at much lower temperatures (<100 °C) compared to other methods.[8] However this procedure requires as much as 20 mol % of the expensive $Pd(O_2CCF_3)_2$ catalyst and 10 equiv of trifluoroacetic acid co-solvent.

Very recently, Ag salts were highlighted to have an important role in the protiodecarboxylation of *ortho*-substituted aromatic carboxylic acids.[9] The nature of the *ortho* substituents was reported to be extremely important, as the protiodecarboxylation reactions were activated by strongly electron-donating and -withdrawing groups. These protiodecarboxylation protocols have been lately extended to heteroaromatic carboxylic acids with the ring heteroatom playing the same role as the *ortho* substituent.[10] The results showed that heteroatom played an activating role as though the carboxylic acids with β or γ heteroatoms were not activated unless an *ortho* electron-withdrawing substituent was present.

We became interested in protiodecarboxylation reaction of coumarin-3-carboxylic acids in the context of our research on decarboxylative cross-coupling reactions of this structural motifs.[11]

Decarboxylation reactions in coumarin-3-carboxylic acid derivatives are useful for the removal of surplus carboxylate groups left behind as a result of ring-closure reactions of active methylenes and arylaldehydes as a convenient procedure for their synthesis.[12]

Whilst highly activated β-oxo carboxylic acids, decarboxylate reasonably easily even in the absence of a catalyst, protiodecarboxylation reaction of coumarin-3-carboxylic acids revealed to be a challenging goal. The reports on protiodecarboxylation of coumarins via thermal decarboxylations, suffer from the same problems, namely, the requirement for extremely high temperatures.[13]

We hypothesized that decarboxylation protocols may be applied to protiodecarboxylation of coumarin-3-carboxylic acids, which would be of great value in the synthesis of important biological active products.[14] Herein, we set out to explore a mild and operationally

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simple procedure for the Ag-catalyzed protiodecarboxylation of a range of diversely functionalized coumarin-3-carboxylic acids.

2. Results and discussion

To test the feasibility of this reaction, we initially examined the protiodecarboxylation reaction of coumarin-3-carboxylic acid **1a** under various reaction conditions directing our investigations toward decreasing the high temperature required in protiodecarboxylation reactions. Accordingly, the carboxylic acid **1a** was first treated with $PdCl_2$ (10 mol %) in DMSO at 160 °C. To our delight, protiodecarboxylated product **2a** was obtained in 59% yield (Table 1, entry 1). Replacing $PdCl_2$ with other palladium sources, such as $Pd(OAc)_2$, Pd $(OH)_2$/C, and $Pd(dba)_2$ did not lead to much improvement in reactivity (Table 1, entries 2–4). In order to promote efficient protonation of the metal arene intermediate, which is produced in the course of reaction, we next examined the effect of introducing additional acid co-catalysts. The results showed that the use of 5% TFA improved the yield of the desired product to 70% (Table 1, entry 5). Gratifyingly, application of 5% AcOH as a milder acid additive gave similar results and hence was chosen for later investigations (Table 1, entry 6). Inspired by the recent developments in silver-promoted protiodecarboxylation reactions, we replaced palladium salts with silver salts. Accordingly, the screening reactions were performed with respect to Ag(I) salts, such as AgOAc and Ag_2CO_3, which the later was proved to be the superior one (Table 1, entries 7–8). We were delighted to see that under these conditions, the reaction readily proceeded at 100 °C, a much lower temperature compared to earlier methods (Table 1, entries 9–11). Our attempts to lower the temperature to 80 °C led to lower yield of the desired product (Table 1, entry 12). The yield could finally be improved up to an excellent 89% when using DMA as the solvent (84% isolated yield, Table 1, entry 11 and Table 2, entry 1). A further increase in catalyst's amount did not improve the yield beyond that observed with 5 mol %. The optimized reaction conditions was established as carboxylic acid (1 equiv), Ag_2CO_3 (10 mol %), AcOH (5 mol %) in DMA (0.5 M) in a sealed tube at 100 °C for 16 h.

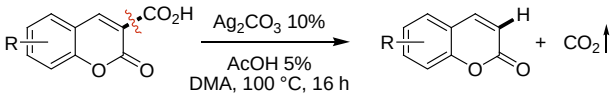
Table 1
Screening of the reaction conditions for protiodecarboxylation of coumarin-3-carboxylic acid **1a**[a]

Entry	Catalyst	Co-catalyst	Solvent	Temp (°C)	Yield[b] (%)
1	$PdCl_2$	—	DMSO	160	59
2	$Pd(OAc)_2$	—	DMSO	160	60
3	$Pd(OH)_2$/C	—	DMSO	160	38
4	$Pd(dba)_2$	—	DMSO	160	42
5	$Pd(OAc)_2$	TFA	DMSO	160	70
6	$Pd(OAc)_2$	AcOH	DMSO	160	71
7	AgOAc	AcOH	DMSO	160	66
8	Ag_2CO_3	AcOH	DMSO	160	79
9	Ag_2CO_3	AcOH	DMA	160	85
10	Ag_2CO_3	AcOH	DMA	120	86
11	**Ag_2CO_3**	**AcOH**	**DMA**	**100**	**89 (84)**[c]
12	Ag_2CO_3	AcOH	DMA	80	78

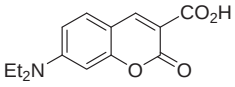
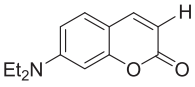
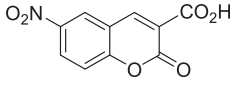
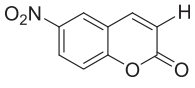
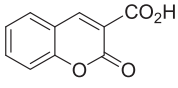
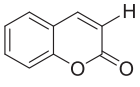
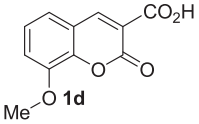
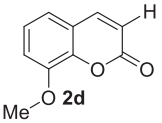
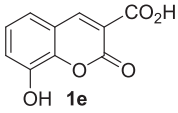
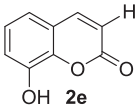
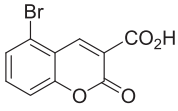
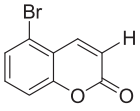
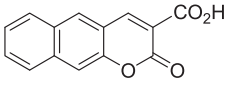
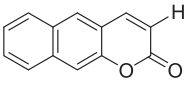
[a] All reactions were run under the following conditions: coumarin-3-carboxylic acid **1a** (1 equiv), catalyst (10 mol %) and co-catalyst (5 mol %) in appropriate solvent (0.5 M) were heated in a sealed tube for 16 h.
[b] GC yields.
[c] Isolated yield in parentheses.

Next, we investigated the scope of the reaction using various substituted coumarin-3-carboxylic acids. We were pleased to find that these conditions were compatible with a range of electron-withdrawing and electron-donating substituents. The conditions were sufficiently mild to be tolerated by a number of functionalities including nitro and hydroxyl groups. The coumarin-3-carboxylic acid with a 6-nitro group **1b**, led to a quantitative yield of protiodecarboxylation product **2b** (90% yield, Table 2, entry 2). It is noteworthy that even when an unprotected hydroxyl group was introduced, a good yield of corresponding coumarin **2e** was obtained (Table 2, entry 5). The un-activated arene carboxylic acids **1c** and **1d**, gave rise to the corresponding decarboxylated products in good to moderate yields with the remainder being unreacted starting materials (Table 2, entries 3 and 4). A further increase in reaction time did not lead to any improvement in the yields. On the other hand, a good yield of 58% of **2f** was obtained using an arene carboxylic acid bearing the mildly electron-withdrawing bromo group (Table 2, entry 6). Finally, the generality of the reaction was extended to benzocoumarin-3-carboxylic acid **1g**, which resulted the corresponding product **2g** in 67% yield (Table 2, entry 7).

Table 2
Scope for the silver-catalyzed protiodecarboxylation of coumarin-3-carboxylic acids **1a–g**

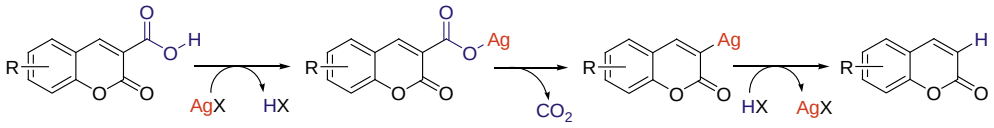


1a-1g **2a-2g**

Entry	Aryl iodide	Product	Yield[a] (%)
1	 **1a**	 **2a**	84
2	 **1b**	 **2b**	90
3	 **1c**	 **2c**	63
4	 **1d**	 **2d**	47
5	 **1e**	 **2e**	65
6	 **1f**	 **2f**	58
7	 **1g**	 **2g**	67

[a] Isolated yields.

A plausible mechanism for the silver-promoted decarboxylation of coumarin-3-carboxylic acids, based on the findings of Larrosa et al.[9,10] is outlined in Scheme 1. The reaction is proposed to proceed via an initial acid–base reaction of carboxylic acid and the silver salt followed by decarboxylation to a silver arene intermediate, which subsequently undergoes protiodemetallation. The co-catalyst acids are supposed to play an important role in promoting efficient protonation of the silver arene intermediates.



Scheme 1. A plausible mechanism for the Ag-catalyzed protiodecarboxylation of coumarin-3-carboxylic acids.

3. Conclusion

In summary, we have developed a mild and efficient protocol for silver-catalyzed decarboxylations of coumarin-3-carboxylic acids. This procedure proved to be generally applicable for smooth protiodecarboxylation of diversely functionalized coumarin-3-carboxylic acids and a variety of substituents were tolerated under the reaction conditions. Operational simplicity, the lower toxicity of Ag (I) salts and reduced reaction temperatures and therefore wide substrate compatibility are the advantages of this method.

4. Experimental section

4.1. General

Anhydrous solvents were used. Metal catalysts were commercially available and used as received. The protiodecarboxylation reactions were carried out in an oil bath using Microwave vials (2–5 mL). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on 300 and 75 MHz spectrometers, respectively, using $CDCl_3$ and acetone-d_6 as the NMR solvents. ^{1}H NMR spectra are referenced to tetramethylsilane (0.00 ppm) and ^{13}C NMR spectra are referenced from the solvent central peak. Chemical shifts are given in parts per million. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

4.2. Synthesis of 2*H*-chromen-2-ones 2a–2g via protiodecarboxylation of coumarin-3-carboxylic acids

*4.2.1. 7-(Diethylamino)-2H-chromen-2-one (**2a**)*[15]. A vial equipped with a stir bar was charged with 7-(diethylamino)-2-oxo-2*H*-chromene-3-carboxylic acid **1a** (0.052 g, 0.2 mmol), Ag_2CO_3 (10 mol %), and ACOH (5 mol %) and DMA (0.5 M) was added and the vial was capped. The resulting mixture was heated in an oil bath at 100 °C for 16 h, cooled then filtered through a short plug of silica and the solvent was removed under vacuo. Purification of the crude product by flash column chromatography (20% EtOAc/hexane) afforded the corresponding product **2a** (0.036 g, 84%) as an orange solid, mp 87–89 °C; R_f (20% EtOAc/hexane) 0.40; δ_H (300 MHz, $CDCl_3$) 7.50 (1H, d, *J* 10.6 Hz, C*H*=), 7.24 (1H, d, *J* 8.8 Hz, Ph), 6.55 (1H, dd, *J* 8.8, 2.5 Hz, Ph), 6.48 (1H, d, *J* 2.5 Hz, Ph), 6.00 (1H, d, *J* 10.6 Hz, =C*H*), 3.38 (4H, q, *J* 7.1 Hz, CH_2CH_3), 1.22 (6H, t, *J* 7.1 Hz, *Me*); δ_C (75 MHz, $CDCl_3$) 162.6, 157.1, 151.1, 144.1, 129.2, 109.4, 109.1, 108.6, 97.8, 45.2, 12.8.

*4.2.2. 6-Nitro-2H-chromen-2-one (**2b**)*[16]. Operation as above with 6-nitro-2-oxo-2*H*-chromene-3-carboxylic acid **1b** (0.047 g, 0.2 mmol) compound **2b** (0.034 g, 90%) was obtained as yellowish solid, mp 181–182 °C; R_f (20% EtOAc/hexane) 0.33; δ_H (300 MHz, $CDCl_3$) 8.04 (1H, dd, *J* 7.35, 1.35 Hz, Ph), 7.93 (1H, d, *J* 1.35 Hz, Ph), 7.78 (1H, d, *J* 9.12 Hz, C*H*=), 7.25 (1H, d, *J* 7.35 Hz, ph), 6.40 (1H, d, *J* 9.12 Hz, =C*H*); δ_C (75 MHz, $CDCl_3$) 163.3, 159.2, 150.5, 148.6, 129.0, 113.4, 112.0, 111.5.

*4.2.3. 2H-Chromen-2-one (**2c**)*[16]. Operation as above with 2-oxo-2*H*-chromene-3-carboxylic acid **1c** (0.038 g, 0.2 mmol) compound **2c** (0.018 g, 63%) was obtained as colorless needles, mp 68–70 °C; R_f (20% EtOAc/hexane) 0.43; δ_H (300 MHz, $CDCl_3$) 7.85 (1H, d, *J* 8.90 Hz, C*H*=), 7.44–7.58 (2H, m, Ph), 7.38–7.22 (2H, m, Ph), 6.70 (1H, d, *J* 8.90 Hz, =C*H*); δ_C (75 MHz, $CDCl_3$) 160.8, 154.1, 143.5, 131.9, 127.9, 124.5, 118.9, 116.7, 116.6.

*4.2.4. 8-Methoxy-2H-chromen-2-one (**2d**)*[17]. Operation as above with 8-methoxy-2-oxo-2*H*-chromene-3-carboxylic acid **1d** (0.044 g, 0.2 mmol) compound **2d** (0.017 g, 47%) was obtained as colorless needles, mp 86–87 °C; R_f (20% EtOAc/hexane) 0.26; δ_H (300 MHz, $CDCl_3$) 7.60 (1H, d, *J* 10.1 Hz, C*H*=), 7.03 (1H, d, *J* 8.0 Hz, Ph), 6.92 (1H, d, *J* 8.0 Hz, Ph), 6.90 (1H, dd, *J* 8.0, 1.2 Hz, Ph), 6.27 (1H, d, *J* 10.1 Hz, =C*H*), 3.89 (3H, s, O*Me*); δ_C (75 MHz, $CDCl_3$) 160.5, 147.2, 144.1, 143.6, 124.5, 119.5, 119.4, 116.8, 113.9, 56.3.

*4.2.5. 8-Hydroxy-2H-chromen-2-one (**2e**)*[18]. Operation as above with 8-hydroxy-2-oxo-2*H*-chromene-3-carboxylic acid **1e** (0.041 g, 0.2 mmol) compound **2e** (0.021 g, 65%) was obtained as colorless needles, mp 159–161 °C; R_f (20% EtOAc/hexane) 0.15; δ_H (300 MHz, acetone-d_6) 7.92 (1H, d, *J* 9.6 Hz, C*H*=), 7.11–7.15 (3H, m, Ph), 6.39 (1H, d, *J* 9.6 Hz, =C*H*), 6.13 (1H, s, O*H*); δ_C (75 MHz, acetone-d_6) 160.1, 145.2, 144.8, 143.2, 125.1, 120.5, 119.4, 119.0, 116.9.

*4.2.6. 5-Bromo-2H-chromen-2-one (**2f**)*[16]. Operation as above with 5-bromo-2-oxo-2*H*-chromene-3-carboxylic acid **1f** (0.054 g, 0.2 mmol) compound **2f** (0.026 g, 58%) was obtained as colorless needles, mp 93–95 °C; R_f (20% EtOAc/hexane) 0.52; δ_H (300 MHz, $CDCl_3$) 7.90 (1H, d, *J* 9.1 Hz, C*H*=), 7.71 (1H, dd, *J* 7.1, 1.34 Hz, Ph), 7.34 (1H, dd, *J* 7.1, 1.34 Hz, Ph), 7.25–7.27 (1H, m, Ph), 6.67 (1H, d, *J* 9.1 Hz, =C*H*); δ_C (75 MHz, $CDCl_3$) 160.1, 154.2, 150.0, 142.5, 135.0, 130.6, 119.1, 118.3, 117.4.

*4.2.7. 2H-Benzo[g]chromen-2-one (**2g**)*[19]. Operation as above with 2*H*-benzo[*g*]chromen-2-one-3-carboxylic acid **1g** (0.048 g, 0.2 mmol) compound **2g** (0.026 g, 67%) was obtained as yellowish solid, mp 124–125 °C; R_f (20% EtOAc/hexane) 0.40; δ_H (300 MHz, $CDCl_3$) 8.27 (1H, m, Ph), 8.12 (1H, m, Ph), 8.03 (1H, d, *J* 8.6 Hz, Ph), 8.00 (1H, m, Ph), 7.65 (2H, m, Ph), 7.55 (1H, d, *J* 7.3 Hz, Ph), 6.47 (1H, d, *J* 9.5 Hz, =C*H*); δ_C (75 MHz, $CDCl_3$) 160.1, 151.4, 143.1, 132.1, 131.0, 130.0, 127.0, 125.1, 124.4, 115.8, 113.6.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.019.

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