无过渡金属条件下 α -芳香酮酸与叠氮磷酸二苯酯 脱羧酰胺化制备芳香伯酰胺

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摘要 报道了一种无过渡金属条件下, α -芳香酮酸和叠氮磷酸二苯酯(DPPA)发生脱羧偶联制备芳香伯酰胺的方法。该方法条件温和, 无需惰性气体保护, 各种取代芳香 α -酮酸均可顺利反应得到优良的分离产率, 体现了较好的官能团适应性。克量级实验在该反应条件下也可顺利实现, 以高产率生成目标产物, 同时对反应机理也进行了探究。

关键词 脱羧酰胺化反应; 伯酰胺; 叠氮磷酸二苯酯; α -芳香酮酸; 无过渡金属

Transition-Metal-Free Decarboxylative Amidation of Aryl α -Keto Acids with Diphenylphosphoryl Azide: New Avenue for the Preparation of Primary Aryl Amides

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Abstract In this paper, a novel transition-metal-free decarboxylative amidation of aryl α -keto acids with diphenylphosphoryl azide (DPPA) under mild conditions has been developed. The reaction proceeded smoothly to afford the corresponding primary aryl amide products in good to excellent yields under air and showed excellent functional group tolerance. Gram-scale reaction was also performed to produce the desired product in high yield. In addition, the mechanism of the present reaction was investigated.

Keywords decarboxylative amidation; primary amides; diphenylphosphoryl azide; α -keto acids; transition-metal-free

1 Introduction

Primary aromatic amides are important structural motifs prevalent in a wide range of class of compounds in natural products, materials, pharmaceuticals, agrochemicals and polymers.^[1] In addition, amides are very good functional groups in organic synthesis, because they can be easily transformed into nitriles, primary amines and heterocycles.^[2] Because of their importance, numerous methodologies have been developed for their synthesis. Some examples include ammonolysis of carboxylic acids, rearrangement of aldoximes, metal-catalyzed carbonylation of organohalides with ammonia, direct oxidation of benzyl amines or benzyl alcohol, and hydration of nitriles.^[3] Of

these methods, the ammonolysis of activated carboxylic acid species is still the traditional method for synthesis of primary amides. However, this procedure requires pre-activation of the free carboxylic acid with stoichiometric activating reagents, and corrosive by-products are often generated during the reaction. Thus, the development of greener and more efficient methods to prepare amides from carboxylic acids is still a challenge for synthetic organic chemistry.

On the other hand, carboxylic acids are readily available, and are usually used as key substrates for organic synthesis.^[4] Currently, transition-metal-catalyzed decarboxylative couplings have attracted much attention due to readily accessible starting materials, simple operation, and

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clean byproduct (CO_2 as the only byproduct). It should be noted that the preparation of functionalized acyl compounds via the decarboxylation of α -keto acids is of great interest.^[5] Since the first report on Cu/Pd-catalyzed decarboxylative acylation of aryl bromides with α -keto acids, which was considered as an acyl anion equivalent to afford diaryl ketones,^[5a] extensive studies have been carried out. So far, α -keto acids have been successfully utilized as acyl nucleophiles in transition-metal-catalyzed decarboxylative coupling reactions to form C—C bonds.^[4b,6] However, the formation of C—N bonds, which led to much more efficient protocols for the desired target molecules, has received less attention. In 2014, Lei's group^[7] developed a visible-light-mediated decarboxylation/oxidative amidation of α -keto acids with amines for the formation of amides (Scheme 1, a). In 2016, Xu's group^[8] reported two approaches for the same transformation by photocatalysis and Ag catalysis, respectively (Scheme 1, b). In the same year, Wang's group^[9] described a decarboxylative amidation of α -keto acids with *N*-substituted *N*-heteroarene-2-carboxamides in the presence of $\text{Pd}(\text{OAc})_2$ and $\text{K}_2\text{S}_2\text{O}_8$ (Scheme 1, c). And then, Yotphan's group^[10] demonstrated a copper-catalyzed oxidative decarboxylative coupling of α -keto acids with NH-sulfoximines (Scheme 1, d). In addition, Ilangoan and co-workers reported a one-pot procedure for the conversion of 2-iodo/2-nitro benzoic acids into the corresponding anilines using tosyl azide as the nitrogen resource. And the substituent of 2-iodo or 2-nitro in benzoic acids is the necessary group for the success of this reaction^[11] (Scheme 1, e).

These reactions are mostly suitable for preparation of secondary and tertiary amides or primary anilines via decarboxylative amidation strategies from α -keto acids or benzoic acids, but the direct decarboxylative coupling of α -keto acids with azide reagents to form primary amides has never been reported. Inspired and encouraged by these pioneering studies and with part of our continuous interest in C—N bond formation reaction,^[12] we herein report a novel transition-metal-free decarboxylative amidation of α -keto acids with diphenylphosphoryl azide (DPPA) to preparation primary aryl amides under mild conditions (Scheme 1, f).

2 Results and discussion

In our initial experiment, phenylglyoxylic acid (**1a**) and DPPA were chosen as the model substrates to optimize reaction conditions including azide reagents and its dosage, bases, solvent, reaction temperature and time. As shown in Table 1, the reaction between **1a** and DPPA in the presence of 2 equiv. of K_2CO_3 in *N,N*-dimethylformamide (DMF) at 100 °C for 24 h afforded benzamide (**3a**) in 75% yield (Entry 1). Azide reagents screening showed that DPPA gave the best isolate yield of the desired product, while tosyl azide and TMSN_3 gave trace yield or no reaction (Entries 2 and 3). Decreasing the quantity of DPPA led to lower yield (Entry 4). Subsequently, the base was found to

Previous work

(a) Lei's work^[7]

(b) Xu's work^[8]

(c) Wang's work^[9]

(d) Yotphan's work^[10]

(e) Ilangoan's work^[11]

(f) This work

Scheme 1 Previous decarboxylative amidation of α -keto acids methods and our work

have an important effect on the reactivity (Entries 1 and 5~7). Among the bases tested, K_3PO_4 was found to be the best with 91% yield. Investigation of a variety of solvent, including DMF, DMSO, NMP, H_2O and mixed solvent DMF/ H_2O (*V*:*V* = 1:1), indicated DMF to be the best one (Entries 6 and 8~11). Furthermore, lower yields were observed when decreasing reaction temperature or shortening reaction time (Entries 12 and 13). In summary, the optimal conditions for this decarboxylative amidation were established from the reaction of **1a** (1 equiv.) with DPPA (2 equiv.) in the presence K_3PO_4 (2.0 equiv.) in 2 mL of DMF at 100 °C for 24 h, affording **3a** in 91% yield (Entry 6).

With the optimized reaction conditions in hand, the sub-

Table 1 Screening reaction conditions for decarboxylative amidation of phenylglyoxylic acid with azide reagents^a

Entry	Azide	Base	Solvent	Yield ^b /%
1	DPPA	K ₂ CO ₃	DMF	75
2	TsN ₃	K ₂ CO ₃	DMF	trace
3	TMSN ₃	K ₂ CO ₃	DMF	NR
4	DPPA	K ₂ CO ₃	DMF	70 ^c
5	DPPA	Cs ₂ CO ₃	DMF	77
6	DPPA	K₃PO₄	DMF	91
7	DPPA	NaHCO ₃	DMF	73
8	DPPA	K ₃ PO ₄	DMSO	75
9	DPPA	K ₃ PO ₄	NMP	58
10	DPPA	K ₃ PO ₄	H ₂ O	NR
11	DPPA	K ₃ PO ₄	DMF/H ₂ O (V : V = 1 : 1)	NR
12	DPPA	K ₃ PO ₄	DMF	71 ^d
13	DPPA	K ₃ PO ₄	DMF	76 ^e

^a Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), base (1.0 mmol), solvent (2 mL), 100 °C, 24 h; ^b Isolated yield; ^c DPPA (0.6 mmol); ^d 80 °C; ^e 12 h.

Table 2 One pot synthesis of primary amides from α -keto acids and DPPA^a

Product	Yield (%)
3a (R = H)	91%
3b (R = 4-OMe)	90%
3c (R = 4-Me)	92%
3d (R = 4-F)	95%
3e (R = 4-Cl)	79%
3f (R = 4-Br)	80% ^b
3g (R = 4-I)	85% ^b
3h (R = 4-CF ₃)	72% ^c
3i (R = 4-NO ₂)	80% ^c
3j (R = 3-Me)	87%
3k (R = 3-I)	71% ^c
3l (R = 3-F)	93%
3m (R = 3-NO ₂)	75% ^c
3n (R = 2-Br)	78% ^c
3o (3,4,5-trimethoxyphenyl)	78%
3p (3,4-dimethylphenyl)	79% ^c
3q (2,4-dichlorophenyl)	78%
3r (1-naphthyl)	85%
3s (2-naphthyl)	78% ^d
3t (thiophen-2-yl)	93%
3u (2-oxo-2-phenylacetic acid derivative)	trace
3v (2-oxo-2-phenylacetic acid derivative)	trace

^a Reaction conditions: **1** (0.5 mmol), DPPA (1.0 mmol), K₃PO₄ (1.0 mmol), DMF (2 mL), 100 °C, 24 h; isolated yield; ^b DPPA (1.5 mmol); ^c 48 h.

strate scope of this decarboxylative amidation of α -keto acids with DPPA was next explored (Table 2). The results indicated that various functional groups, including both electron-donating and electron-withdrawing groups on the

para-position of the benzene rings in 2-oxo-2-arylacetic acids were well tolerated, and the desired amidation products were obtained in good to excellent yields. Notably, the electron-donating groups, such as MeO and Me, exhibited higher activity, providing the corresponding products (**3b**~**3c**) in 90% and 92% yields. On the other hand, the electron-withdrawing groups, such as halogen groups (Cl, F, Br and I), CF₃ and NO₂ showed good reactivity to the reaction, affording the desired products (**3d**~**3i**) in 72%~95% yields, which provide useful handles for further transformations through traditional reactions. Furthermore, it was found that *meta*-substituted 2-oxo-2-phenylacetic acids were also reacted well to generate **3j**~**3m** in 71%~93% yields. Notably, *ortho*-substituted substrate underwent this decarboxylation process smoothly to afford the corresponding product in 78% yields (**3n**). To our delight, 3,4- or 2,4-disubstituted 2-oxo-2-phenylacetic acids can react with DPPA in 78%~79% yields under the present conditions (**3o**~**3q**). It should be noted that when 2-(naphthalen-1-yl)-2-oxoacetic acid and 2-(naphthalen-2-yl)-2-oxoacetic acid were employed to react with DPPA, the corresponding imides **3r** and **3s** were afforded in 85% and 78% yields, respectively. Surprisingly, heterocyclic 2-oxo-2-(thiophen-2-yl)acetic acid could display good reactivity and provide the desired product **3t** in 93% yield without prolonging the reaction time or raising the reaction temperature. Unfortunately, the reactions of aliphatic α -keto acids did not work well under the standard condition because of low conversion (**3u** and **3v**).

To evaluate the scalability of the catalytic system, 10 mmol scale of phenylglyoxylic acid was used to perform the decarboxylative amidation, and the product **3a** was obtained in 81% yield, which provides a reference for industrial production (Scheme 2).

Scheme 2 Gram-scale synthesis of **3a**

In order to understand the mechanism of the present reaction, radical inhibition experiments were performed (Scheme 3). When 2 equiv. of radical scavenger such as 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO) or 2,6-bis-(1,1-dimethylethyl)-4-methyl-phenol (BHT) was added to the mixture solution, the decarboxylative amidation reaction proceeded as normal with comparable efficiency and gave **3a** in similar yield of the standard condition. These results suggested that the reaction might not proceed through a radical decarboxylation. Therefore, it is believed that the reaction is carried out through a Curtius rearrangement pathway (Scheme 4). First, α -keto acid reacts with DPPA to form acyl azide intermediate **I** under the action of base, and then **I** loses one molecule of N₂ to form azobenzene intermediate **II** under heating condition, **II**

rearranges to form benzoyl isocyanate intermediate **III** through intramolecular rearrangement, followed by reaction with water to the unstable acylcarbamic acid derivative **IV** which will undergo decarboxylation to form benzamide and release one molecule of CO₂.

Scheme 3 Validation experiments

Scheme 4 Plausible mechanism

3 Conclusions

In conclusion, we have established a simple, transition-metal-free protocol for the decarboxylative amidation of α -keto acids with DPPA. This reaction provides a new synthetic method and idea for the synthesis of primary aryl amides, and twenty aromatic primary amides were obtained in 71%~95% yields. The convenient operation, no transition-metal catalysts and scalability are the salient features, which render this method viable for both academic research and industrial processes.

4 Experimental section

4.1 Materials and instruments

Commercial reagents were purchased from Adamas, Ark Pharm, Innochem, Acros Organics and used as received unless otherwise noted. DMF was purchased from Fuyu Fine Chemical Co., Ltd, and was distilled under reduced pressure before used. The α -keto acids **1a**, **1t**, **1u** and **1v** were obtained from commercial suppliers, and the others were prepared from oxidation of corresponding methyl ketones by SeO₂ according to the reported procedure.^[13] All reactions were carried out under air atmosphere. NMR spectra were measured on a Bruker Avance III HD 400 spectrometer. ¹H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ¹³C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Column chromatography was performed with silica gel (200~300 mesh) purchased from Qingdao Haiyang

Chemical Co. Ltd.

4.2 General procedure for decarboxylative amidation

α -Keto acid (0.5 mmol), DPPA (1.0 mmol), and K₃PO₄ (1.0 mmol) were placed in a schlenk tube equipped with a stirring bar. The solvent DMF (2 mL) was added under air atmosphere. The reaction was carried out at 100 °C for 24 or 48 h. After the reaction, the mixture was quenched with saturated sodium bicarbonate (10 mL) and extracted with ethyl acetate (10 mL $\times$ 3). The organic layers were combined and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel [*V*(petroleum ether)/*V*(ethyl acetate)=2/1] to afford target products **3a**~**3t**.

Benzamide (3a):^[14] 91% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.98 (s, 1H), 7.90~7.86 (m, 2H), 7.57~7.49 (m, 1H), 7.49~7.42 (m, 2H), 7.37 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 168.4, 134.7, 131.7, 128.7, 127.9.

4-Methoxybenzamide (3b):^[15] 90% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.97~7.74 (m, 3H), 7.19 (s, 1H), 7.05~6.91 (m, 2H), 3.80 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.9, 162.0, 129.8, 127.0, 113.8, 55.8.

4-Methylbenzamide (3c):^[15] 92% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.90 (s, 1H), 7.78 (d, *J*=8.1 Hz, 2H), 7.25 (d, *J*=8.0 Hz, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 168.3, 141.5, 132.0, 129.2, 128.0, 21.4.

4-Fluorobenzamide (3d):^[15] 95% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.00 (s, 1H), 7.97~7.92 (m, 2H), 7.40 (s, 1H), 7.31~7.25 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.3, 164.4 (*J*=246.8 Hz), 131.2 (*J*=2.9 Hz), 130.6 (*J*=9.0 Hz), 115.5 (*J*=21.6 Hz).

4-Chlorobenzamide (3e):^[15] 79% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.05 (s, 1H), 7.92~7.88 (m, 2H), 7.55~7.51 (m, 2H), 7.47 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.3, 136.5, 133.5, 129.9, 128.8.

4-Bromobenzamide (3f):^[15] 80% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.05 (s, 1H), 7.84~7.80 (m, 2H), 7.69~7.65 (m, 2H), 7.46 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.4, 133.9, 131.7, 130.1, 125.5.

4-Iodobenzamide (3g):^[15] 85% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.03 (s, 1H), 7.84 (d, *J*=8.4 Hz, 2H), 7.65 (d, *J*=8.4 Hz, 2H), 7.43 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.7, 137.6, 134.2, 129.9, 99.4.

4-Trifluoromethylbenzamide (3h):^[16] 72% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.24 (s, 1H), 8.11 (d, *J*=8.0 Hz, 2H), 7.88 (d, *J*=8.0 Hz, 2H), 7.67 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.2, 138.6 (d, *J*=0.9 Hz), 131.6 (q, *J*=1.6 Hz), 128.8, 125.7 (q, *J*=3.9 Hz), 123.1.

4-Nitrobenzamide (3i):^[17] 80% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.31 (d, *J*=8.8 Hz, 3H), 8.11 (d, *J*=8.8 Hz, 2H), 7.74 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 166.7, 149.5, 140.5, 129.4, 123.9.

3-Methylbenzamide (3j):^[14] 87% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.96 (s, 1H), 7.75 (s, 1H), 7.73~7.70 (m, 1H), 7.39~7.37 (m, 2H), 7.35 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 168.5, 137.9, 134.7, 132.2, 128.5, 125.1, 21.4.

3-Iodobenzamide (**3k**):^[18] 71% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.86 (s, 1H), 7.64 (d, $J=8.0$ Hz, 1H), 7.56 (s, 1H), 7.43~7.40 (m, 2H), 7.36~7.32 (m, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 169.5, 139.8, 133.2, 131.1, 129.0, 128.0, 119.1.

3-Fluorobenzamide (**3l**):^[19] 93% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.07 (s, 1H), 7.73 (d, $J=7.6$ Hz, 1H), 7.69~7.65 (m, 1H), 7.54~7.48 (m, 2H), 7.40~7.35 (m, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 166.9 (d, $J=2.4$ Hz), 162.4 (d, $J=242.5$ Hz), 137.1 (d, $J=6.6$ Hz), 130.8 (d, $J=7.9$ Hz), 124.1 (d, $J=2.7$ Hz), 118.6 (d, $J=21.1$ Hz), 114.7 (d, $J=22.4$ Hz).

3-Nitrobenzamide (**3m**):^[20] 75% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.43 (s, 1H), 7.36~7.29 (m, 2H), 7.00 (d, $J=7.6$ Hz, 1H), 5.85 (s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 150.6, 149.2, 130.4, 120.4, 110.2, 107.5.

2-Bromobenzamide (**3n**):^[15] 78% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.86 (s, 1H), 7.65 (d, $J=8.0$ Hz, 1H), 7.56 (s, 1H), 7.44~7.40 (m, 2H), 7.37~7.30 (m, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 169.5, 139.8, 133.2, 131.1, 129.0, 128.0, 119.1.

3,4-Dimethoxybenzamide (**3o**):^[16] 78% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90 (s, 1H), 7.49 (d, $J=8.0$ Hz, 2H), 7.26 (s, 1H), 7.02 (s, 1H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 167.9, 151.7, 148.6, 127.0, 121.2, 111.4, 111.2, 56.0.

3,4-Dimethylbenzamide (**3p**):^[17] 79% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.84 (s, 1H), 7.67 (d, $J=1.6$ Hz, 1H), 7.59 (dd, $J=7.6, 1.6$ Hz, 1H), 7.21 (s, 1H), 7.19 (d, $J=7.6$ Hz, 1H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 168.4, 140.2, 136.5, 132.3, 129.7, 129.1, 125.4, 19.9, 19.8.

2,4-Dichlorobenzamide (**3q**):^[21] 78% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.93 (s, 1H), 7.67 (t, $J=1.2$ Hz, 2H), 7.47 (d, $J=1.2$ Hz, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 167.7, 136.5, 134.7, 131.4, 130.5, 129.6, 127.7.

α -Naphthalamide (**3r**):^[22] 85% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.37~8.35 (m, 1H), 8.05~7.99 (m, 3H), 7.96 (dd, $J=7.2, 1.2$ Hz, 1H), 7.63 (d, $J=1.6$ Hz, 1H), 7.62~7.55 (m, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 171.1, 135.1, 133.7, 130.2, 130.1, 128.6, 127.1, 126.6, 126.1, 125.6, 125.4.

β -Naphthalamide (**3s**):^[22] 78% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.51 (s, 1H), 8.16 (s, 1H), 8.02 (dd, $J=7.2, 2.4$ Hz, 1H), 8.00~7.97 (m, 3H), 7.64~7.57 (m, 2H), 7.49 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 168.4, 134.6, 132.6, 132.1, 129.3, 128.3, 128.2, 128.1, 128.0, 127.1, 124.9.

Thiophene-2-carboxamide (**3t**):^[14] 93% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.96 (s, 1H), 7.75~7.73 (m, 2H), 7.38 (s, 1H), 7.13 (q, $J=4.2$ Hz, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 163.4, 140.8, 131.4, 129.1, 128.3.

Supporting Information The ^1H NMR and ^{13}C NMR

spectra of products **3a**~**3t**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

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