Rhodium-Catalyzed C(sp²)−H Alkoxycarbonylation/Acylation of Indolines with Anhydrides as a Carbonyl Source

Hirotugu Suzuki, Fumito Sasamori, and Takanori Matsuda

ABSTRACT: We developed rhodium-catalyzed alkoxycarbonylation/acylation of indolines using anhydrides as a safe and easy-to-handle carbonyl source. This catalytic process represents an additive- and CO-free carbonylation, establishing a simple and straightforward protocol for synthesizing C7-carbonylated indolines. Notably, this reaction provides a successful example of C−H acylation of indolines that results in the formation of α-branched ketones, which were difficult to prepare by previously reported analogous catalytic reactions.

C7-Carbonylated indoles and their derivatives are an important class of biologically active compounds found in many natural products, pharmaceuticals, and agrochemicals (Scheme 1).1 Common reactions to access C7-carbonylated indoles are palladium-catalyzed carbonylation of 7-haloindoles using carbon monoxide (CO),2 Stille coupling using (1-ethoxyvinyl)stannane,3 and nucleophilic addition of C7-metalated indoles to carbonyl donors.4 Although these well-established protocols provide a reliable route to C7-carbonylated indoles, the prefunctionalization of starting materials makes the reaction less attractive. Moreover, these reactions usually require air- and moisture-sensitive organometallics and harmful reagents. Thus, the development of a simple and efficient procedure to access C7-carbonylated indoles is highly desirable.5

C(sp²)−H functionalization of indolines is one of the most straightforward synthetic pathways for C7-functionalized indoles,6,7 leading to the investigation of a variety of organic transformations, including carbonylation reactions. In 2002, Chatani et al. reported ruthenium-catalyzed carbonylation of indolines with CO and alkenes.8 Subsequently, the oxidative amino- and alkoxycarbonylation of indolines under a CO atmosphere has been reported by other groups.9 In contrast, C(sp²)−H carbonylation of indolines using various carbonyl sources such as azodicarboxylates,10 isocyanates,11 α-keto acids,12 aldehydes,13 1,2-diketones,14 and glyoxalates15 has been studied under CO-free conditions (Scheme 2a). Although these carbonyl sources are less toxic and easy to handle, the use of an external additive such as an oxidant and a base limits their application by producing a stoichiometric amount of unwanted byproducts. Consequently, this complicates the experimental procedure and narrows the substrate scope under oxidative or basic reaction conditions. Despite these critical problems, the additive-free C(sp²)−H carbonylation of indolines is yet to be addressed. We hypothesized that the use of dicarbonates and carboxylic acid anhydrides as a carbonyl source may provide a solution for the additive-free C−H carbonylation of indolines.16,17 Herein, we describe the additive-free C7-selective carbonylation of indolines using dialkyl dicarbonates and carboxylic acid anhydrides as a safe and easy-to-handle carbonyl source (Scheme 2b).

First, the ethoxycarbonylation of 1-(pyrimidin-2-yl)indoline (1a) as a model substrate was investigated (Table 1). An initial
reaction was performed using diethyl dicarbonate (2a) as an ethoxycarbonyl source in the presence of [Rh(cod)2]OTf. The reaction was conducted at 100 °C for 18 h and yielded the desired indoline-7-carboxylic acid ester 3aa (entry 1). Based on these results, other rhodium catalysts such as [RhCl(cod)]2, RhCl(PPh3)3, [RhCl(CO)2]2, Rh(acac)(CO)2, [Cp*RhCl2]2, and [Cp*Rh(MeCN)3](SbF6)2 were tested; [RhCl(CO)2]2 proved to be the optimal catalyst for this process (entries 2–7). Acetonitrile gave the best results among the solvents examined (entries 8–12). A control experiment revealed that the rhodium catalyst was essential for this reaction (entry 13).

With the optimized reaction conditions in hand, the additive-free alkoxycarbonylation using various indoline derivatives was investigated (Table 2). Indolines bearing a methyl and a phenyl group at the 2- or 3-position resulted in the formation of the desired indoline-7-carboxylic acid esters in good to high yields (3ba–da). Introduction of a methyl group at the 4-position did not influence the reactivity (3ea). Indolines bearing electron-donating and electron-withdrawing substituents at the C5 position delivered the desired products in 86–91% yields (3fa–ia). Although a 6-fluoro indoline produced the desired product in high yield (3ja), the reaction of a 6-methyl indoline was sluggish presumably due to steric hindrance (3ka). A carbazole transformed into monoester 3la in moderate yield (36%) along with a small amount (10%) of the double alkoxycarbonylation product. Gratifyingly, 1a was coupled with di-tert-butyl dicarbonate to provide a good yield of 3ab.

To demonstrate the efficacy of this transformation, the reaction of 1a with 2a in 1,4-dioxane was performed on a 5 M scale. The standard conditions: 1a (0.2 mmol), 2a (0.3 mmol), and [RhCl(CO)2]2 (2.5 mol %) in MeCN (0.5 mL) at 100 °C for 18 h. Isolated yields represent the average of two runs. *Yield of the double alkoxycarbonylation product. 2.0 equiv of Boc2O was used.

Table 2. Substrate Scope of Indolines

| Entry | Rh catalyst | Solvent | Yield (%) |
|-------|-------------|---------|-----------|
| 1     | [RhCl(cod)]2OTf | 1,4-dioxane | 25        |
| 2     | [RhCl(cod)]2 | 1,4-dioxane | 83        |
| 3     | RhCl(PPh3)3 | 1,4-dioxane | 89        |
| 4     | [RhCl(CO)2]2 | 1,4-dioxane | 86        |
| 5     | Rh(acac)(CO)2 | 1,4-dioxane | 81        |
| 6     | [Cp*RhCl2]2 | 1,4-dioxane | 0         |
| 7     | [Cp*Rh(MeCN)3](SbF6)2 | 1,4-dioxane | 0         |
| 8     | [RhCl(CO)2]2 | THF | 83        |
| 9     | [RhCl(CO)2]2 | toluene | 79        |
| 10    | [RhCl(CO)2]2 | DCE | 91        |
| 11    | [RhCl(CO)2]2 | DMF | 11        |
| 12    | [RhCl(CO)2]2 | MeCN | 99 (88)   |
| 13    | – | MeCN | 0         |

*Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol), and [RhCl(CO)2]2 (5 mol %) in the solvent (0.5 mL) at 100 °C for 18 h. Isolated yields represent the average of two runs. “Yield of the double alkoxycarbonylation product. 2.0 equiv of Boc2O was used.

Table 1. Optimization of Reaction Conditions

| Entry | Rh catalyst | Solvent | Yield (%) |
|-------|-------------|---------|-----------|
| 1     | [Rh(cod)2]OTf | 1,4-dioxane | 25        |
| 2     | [RhCl(cod)]2 | 1,4-dioxane | 0         |
| 3     | RhCl(PPh3)3 | 1,4-dioxane | 0         |
| 4     | [RhCl(CO)2]2 | 1,4-dioxane | 89        |
| 5     | Rh(acac)(CO)2 | 1,4-dioxane | 81        |
| 6     | [Cp*RhCl2]2 | 1,4-dioxane | 0         |
| 7     | [Cp*Rh(MeCN)3](SbF6)2 | 1,4-dioxane | 0         |
| 8     | [RhCl(CO)2]2 | THF | 83        |
| 9     | [RhCl(CO)2]2 | toluene | 79        |
| 10    | [RhCl(CO)2]2 | DCE | 91        |
| 11    | [RhCl(CO)2]2 | DMF | 11        |
| 12    | [RhCl(CO)2]2 | MeCN | 99 (88)   |
| 13    | – | MeCN | 0         |

*Standard conditions: 1a (0.2 mmol), 2a (0.3 mmol), and Rh catalyst (5 mol % of [Rh]) in the solvent (0.5 mL) at 100 °C for 18 h. Yields were determined by 1H NMR analysis using 1,2,4,5-tetramethylbenzene as an internal standard. Value in parentheses indicates isolated yield, which represents the average of two runs.
mmol scale (Scheme 3). The reaction proceeded smoothly to furnish the product 3aa in good yield. The pyrimidyl directing group in the product could be removed in two steps.9b

**Scheme 3. Large-Scale Reaction**

![Scheme 3](image)

A series of control experiments were performed to elucidate the reaction mechanism (Scheme 4). First, H/D exchange experiments were conducted by subjecting 1a with D2O (5.0 equiv) to the standard reaction conditions in the presence or absence of diethyl dicarbonate (2a). A significant H/D scrambling was observed at the C7 position in both cases, which supports the reversibility of the C−H activation step.

**Scheme 4. Control Experiments**

**(a) H/D exchange experiment**

![Scheme 4](image)

**(b) KIE experiment**

![Scheme 4](image)

Next, the C7-selective acylation of indolines using symmetrical carboxylic acid anhydrides was investigated. Although carboxylic acid anhydrides are known to be good acyl sources in the C3-selective Friedel–Crafts acylation of indoles,20 the corresponding C7-acylation has scarcely been reported. This is due to the decarbonylation process that occurs at high temperatures (>130 °C).19 It was assumed that the C7-acylation of indolines using a carboxylic acid anhydride might proceed without decarbonylation if the optimized reaction conditions were applied. The reaction of indoline 1a with acetic anhydride was initially examined under the optimal conditions for the alkoxycarbonylation. Unfortunately, the desired acylated indoline 5aa was obtained in moderate yield along with a small amount of the methylation product, 7-methyl-1-(pyrimidin-2-yl)indoline, which formed via decarbonylation. Thus, the reaction conditions were slightly modified, and the optimal conditions for the acylation were identified as follows: 5 mol % of [Rh(CO)2Cl]2 in DMF at 80 °C for 24 h.21

Subsequently, the scope of acylation with various symmetrical carboxylic acid anhydrides was investigated (Table 3). Indoline 1a was coupled with acetic anhydride and propionic anhydride to form the corresponding 7-acylated indolines 5aa and 5ab, respectively, in good yields. Notably, acylation of 1a with cyclohexanecarboxylic anhydride provides the α-branched ketone 5ac in 79% yield. This is a successful example of the direct catalytic alkacylation of indoles that yields α-branched ketones, for which efficient coupling reactions have not been reported to date.12−15 Benzoic anhydrides and their derivatives also served as good coupling partners for this acylation. Benzoic anhydride reacted smoothly with 1a to afford the desired product 5ad in 78% yield. Methyl-substituted benzoic anhydrides rendered the desired products 5ae−ag with good efficiency. Varying the electronic properties of benzoic anhydrides did not significantly affect the reactivity (5ah−aj). A heteroaroyl group was also introduced into 1a to form...
Table 3. Substrate Scope of Carboxylic Acid Anhydrides

| Reaction conditions: | 1a (0.2 mmol), 4 (0.3 mmol), and [RhCl\((\text{CO})_2\text{Cl}_2\) (5.0 mol %) in DMF (0.5 mL) at 80 °C for 24 h. Isolated yields represent the average of two runs. |
|---------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1a                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2a                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2b                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2c                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2d                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2e                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 2f                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3a                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3b                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3c                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3d                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3e                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 3f                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4a                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4b                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4c                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4d                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4e                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |
| 4f                  | ![Image](https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195)                                                                                                                                      |

“Reaction conditions: 1a (0.2 mmol), 4 (0.3 mmol), and [RhCl\((\text{CO})_2\text{Cl}_2\) (5.0 mol %) in DMF (0.5 mL) at 80 °C for 24 h. Isolated yields represent the average of two runs.”

Sak in good yield. Thus, our additive-free protocol was applied to a variety of anhydrides without any undesired side reactions.

In summary, we performed additive-free alkoxycarbonylation of indolines using dialkyl dicarbonates as the alkoxycarbonyl source. Furthermore, this additive-free protocol was applied to the acylation of indolines with a variety of aliphatic and aromatic carboxylic acid anhydrides. Unlike previously reported catalytic reactions, our reaction system achieved the formation of α-branched ketones via the acylation of indolines. We believe that these findings will advance the catalytic alkoxycarbonylation/acylation of C(sp³)-H bonds under additive- and CO-free conditions.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195.

Experimental procedures, characterization data, and copies of NMR spectra for new compounds (PDF)

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**Notes**

The authors declare no competing financial interest.

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