# Palladium-Catalyzed Carbonation—Diketonization of Terminal Aromatic Alkenes via Carbon—Nitrogen Bond Cleavage for the Synthesis of 1,2-Diketones

Azhong Wang, Huanfeng Jiang,\* and Xianwei Li

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

Supporting Information

**ABSTRACT:** A palladium-catalyzed carbonation-diketonization reaction of terminal alkenes via carbon-nitrogen bond cleavage under an atmosphere of oxygen has been developed. A series of 1,2-diketones were readily prepared from the reaction of aromatic terminal alkenes with nitroalkanes.



The functionalization of the carbon–nitrogen bond is one of the most challenging targets in modern organic synthesis. As a result, only a few examples of the activation of C–N bond have been reported.<sup>1</sup> However, such transformations would be useful and powerful methods in synthetic organic chemistry because many organic molecules contain carbon-nitrogen bonds. Recently, some significant progress in C-C bond formation reactions via C-N bond cleavage has been achieved with sulfonamides,<sup>2</sup> anilines,<sup>3</sup> or amides<sup>4</sup> as the coupling partners. Even so, little attention has been paid to using nitroalkanes as the coupling partner. To the best of our knowledge, only one example of stoichiometric C-N bond activation with nitromethane has been reported.<sup>5</sup> In connection with our interest in the search for new alkene oxidations, herein, for the first time, we present a palladium-catalyzed carbonation-diketonization reaction of terminal alkenes with molecular oxygen as the oxidant to synthesize 1,2-diketone derivatives, which are important structural units and synthetic intermediates in biologically active natural products and medicinal chemistry.6

The investigation was initiated by using the reaction of styrene with MeNO<sub>2</sub> as a model (Table 1). We were pleased to find that 1,2diketone 2a was obtained in the presence of NaOAc or KOAc with PdCl<sub>2</sub> as catalyst, albeit in low yields (entries 1 and 2). It is obvious that a C-N bond cleavage occurred during the process. This inspirited us to examine optimal reaction conditions for carbonation-diketonization of 1a to 2a in order to obtain more satisfactory results. We first examined the influence of base on the reaction. Among various bases screened (such as CsF, CsOAc, Na<sub>2</sub>CO<sub>3</sub>,  $K_2CO_3$ ,  $Cs_2CO_3$ , and  $Ag_2CO_3$ ),  $Na_2CO_3$  was most effective (entries 3-8). Subsequently, different palladium species such as Pd(OAc)<sub>2</sub>, Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>, [Pd(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub>, and Pd(NO<sub>3</sub>)<sub>2</sub> were also tested (entries 9–12), and  $Pd(OAc)_2$  proved to be the more efficient catalyst in this reaction. It has been reported that H<sub>2</sub>O promotes the diketonization of terminal alkynes;<sup>7</sup> therefore, 10 equiv of H<sub>2</sub>O was added in the reaction. In contrast to these previous studies, water was unable to augment this reaction (entry 13). We envisioned that a radical process was possibly involved.

The presence of 10 mol % of 2,2'-azobisisobutyronitrile (AIBN) promoted the yield of **2a** to 71% (entry 14). The use of other frequently employed radical inhibitors in radical reactions, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), failed to give the product (entries 15 amd 16). These results suggest that the reaction may proceed via a radical process. A control experiment showed that no reaction occurred in the absence of Pd catalyst (entry 17). Only trace of the desired product was observed in the absence of a base (entry 18). This indicated that base played an important role in this process.

To demonstrate the efficiency and generality of this process, we have examined this transformation with both electron-poor and electron-rich aromatic terminal alkenes under the optimized reaction conditions as indicated in entry 14 of Table 1, and the results obtained are summarized in Table 2. Styrenes bearing electron-withdrawing and electron-donating para substituents can be transformed into the corresponding products efficiently (2b-h). A chloride at the *meta* position slightly affected the product yield (2i); however, very low yield was obtained when the chloride group was at the *ortho* position (2j). 2-Vinylnaphthalene and 4-vinyldiphenyl were also good substrates for this transformation (2k and 2l). The scope of the palladium-catalyzed carbonation-diketonization reaction was further expanded to a variety of nitroalkanes. To our delight, nitroethane, 1-nitropropane, 1-nitrobutane, and 2-nitropropane also reacted with styrene to give the desired products in good yields (2m-p). However, an attempt to react tert-nitrobutane with styrene was unsuccessful.

To investigate the origin of the oxygen atoms of the 1,2diketone products, an isotopic labeling study with  ${}^{18}O_2$  was performed (eq 1). The reaction was carried out under 1 atm of  $O_2$  to afford **2n** with a MW of 176 when regular  $O_2$  was used and with a MW of 180 when  ${}^{18}O_2$  was used. The isotopic labeling study

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 Table 1. Optimization of Reaction Conditions for the Palladium-Catalyzed Carbonation–Diketonazation of Styrene<sup>a</sup>



entry	base	additive	catalyst	yield <sup><math>b</math></sup> (%)
1	NaOAc		PdCl <sub>2</sub>	17
2	KOAc		PdCl <sub>2</sub>	8
3	CsF		PdCl <sub>2</sub>	0
4	CsOAc		PdCl <sub>2</sub>	trace
5	$Na_2CO_3$		PdCl <sub>2</sub>	36
6	$K_2CO_3$		PdCl <sub>2</sub>	9
7	$Cs_2CO_3$		PdCl <sub>2</sub>	0
8	Ag <sub>2</sub> CO <sub>3</sub>		PdCl <sub>2</sub>	trace
9	$Na_2CO_3$		$Pd(OAc)_2$	48
10	$Na_2CO_3$		$Pd(CH_3CN)_2Cl_2$	13
11	$Na_2CO_3$		$[Pd(CH_3CN)_4]BF_4$	trace
12	$Na_2CO_3$		$Pd(NO_3)_2$	26
$13^d$	$Na_2CO_3$	$H_2O$	$Pd(OAc)_2$	trace
14	$Na_2CO_3$	AIBN <sup>e</sup>	$Pd(OAc)_2$	71 (67)
15	$Na_2CO_3$	$DDQ^{e}$	$Pd(OAc)_2$	0
16	$Na_2CO_3$	TEMPO <sup>e</sup>	$Pd(OAc)_2$	0
17	$Na_2CO_3$	AIBN <sup>e</sup>	none	0
18	none	AIBN <sup>e</sup>	$Pd(OAc)_2$	trace

<sup>*a*</sup> Unless otherwise indicated, all reactions were performed with styrene (1 mmol), Pd cat. (5 mol %), initial pressure of O<sub>2</sub> (8 atm), and base (2 mmol) in 3 mL of MeNO<sub>2</sub>, 120 °C for 20 h. <sup>*b*</sup> Determined by GC analysis of crude reaction mixture, number in parentheses is yield of isolated product based on complete alkene consumption. <sup>*c*</sup> CuCl<sub>2</sub> (10 mol %). <sup>*d*</sup> 10 equiv of H<sub>2</sub>O was added in the reaction. <sup>*e*</sup> 10 mol %.

clearly demonstrated that the oxygen atoms of 2n originated from molecular  $O_2$ .



At this moment, although it is premature to give rationale behind these reactivities, preliminary reaction pathways for the reaction of styrene with nitromethane might be proposed, as shown in Scheme 1. Initially, a methyl radical would be generated from nitromethane in the presence of  $Pd(OAc)_2$  and  $Na_2CO_{3}$ ,<sup>8,9</sup> which selectively adds to styrene to produce intermediate A. Intermediate A would be attacked by O<sub>2</sub> forming superoxide radical **B**.<sup>10</sup> The superoxide radical **B** undergoes [1,4] H abstraction to generate hydroperoxide C, which subsequently transforms to ketone radical D. According to the Russell mechanism,<sup>11</sup> the oxidation of ketone radical D with O2 leads to the formation of  $\alpha$ -hydroxy ketone and 1,2-diketone in equal yields (eq 2). The fact that the  $\alpha$ -hydroxy ketone E can be further converted to 2a under the reaction conditions has been proved (eq 3). It is known that the oxidation of propiophenone  $\mathbf{F}$  can also lead to  $2\mathbf{a}$ ,<sup>12</sup> and we, therefore, suspect that pathway b might be involved in the

Table 2. Palladium-Catalyzed Carbonation-Diketonizationof Terminal Alkenes with Nitroalkanes $^{a}$ 





<sup>*a*</sup> Standard reaction conditions: **1** (1 mmol), Pd(OAc)<sub>2</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol), AIBN (0.1 mmol), nitroalkanes (3 mL), 120 °C, initial pressure of O<sub>2</sub> (8 atm), 20 h. Yields quoted are isolated yields.

Scheme 1. Plausible Reaction Pathways



reaction. However, no reaction was observed using propiophenone as the substrate (eq 4). Therefore, the participation of pathway b can be completely excluded. Further studies are required for the elucidation of detailed mechanism.



In summary, we have developed an unprecedented protocol for the synthesis of 1,2-diketones from alkenes and nitroalkanes through palladium-catalyzed cleavage of C–N bond. A variety of functional groups are compatible with the reaction conditions. The success of the present studies not only provides a powerful method for the construction of new carbonation reactions but also suggests a new strategy for C–N bond activation. Future work will include further elucidation of the mechanism and utilizing nitroalkanes as coupling partners for C–C bond formation.

## EXPERIMENTAL SECTION

**General Procedure.** The reactions were carried out in a 15 mL autoclave.  $Pd(OAc)_2$  (11.2 mg, 0.05 mmol),  $Na_2CO_3$  (212 mg, 2 mmol), AIBN (16.4 mg, 0.1 mmol), nitroalkane (3 mL), and alkene (1 mmol) were added into a 15 mL autoclave in sequence.  $O_2$  was pumped into the autoclave to reach the desired pressure, and the autoclave was then heated by oil bath under magnetic stirring for the desired reaction time. After the reaction finished, the autoclave was allowed to cool to room temperature.  $O_2$  was vented, and the surplus was extracted with EtOAc (30 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure to give crude product. The crude product was purified by chromatography on a silica gel column using light petroleum ether/ethyl acetate (10:1) as eluent.

1-Phenylpropane-1,2-dione (**2a**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ 7.99 (d, *J* = 7.2 Hz, 2 H), 7.62 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 2.50 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  200.9, 191.3, 135.1, 131.8, 130.8, 128.6, 26.5; MS (EI, 70 eV) *m*/*z* 148 (M<sup>+</sup>, 2), 105 (100), 77 (83), 51 (36).

1-(4-Fluorophenyl)propane-1,2-dione (**2b**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.03–8.07 (m, 2 H), 7.11–7.16 (m, 2 H), 2.49 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  200.3, 189.5, 166.8 (d, *J* = 256.3 Hz), 133.5 (d, *J* = 9.6 Hz), 128.5 (d, *J* = 3 Hz), 116.3 (d, *J* = 21.9 Hz), 26.4; MS (EI, 70 eV) *m*/*z* 166 (M<sup>+</sup>, 1), 123 (93), 95 (100), 75 (24).

1-(4-Chlorophenyl)propane-1,2-dione (**2c**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.94 (d, J = 8.0 Hz, 2 H), 7.42 (d, J = 8.4 Hz, 2 H), 2.48 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 200.0, 189.7, 141.4, 131.9, 130.3, 129.3, 26.4; MS (EI, 70 eV) m/z 182 (M<sup>+</sup>, 1), 139 (100), 111 (73), 75 (64), 43 (52).

1-(4-Bromophenyl)propane-1,2-dione (**2d**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.88 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H), 2.50 (s, 3 H);

 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  200.0, 189.9, 132.4, 132.0, 130.8, 130.4, 26.4; MS (EI, 70 eV) m/z 226 (M<sup>+</sup>, 2), 183 (100), 155 (59), 75 (53).

1-(4-(*Trifluoromethyl*)phenyl)propane-1,2-dione (**2e**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.13 (d, J = 8.0 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H), 2.53 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 199.4, 189.6, 135.7 (q, J = 32.5 Hz), 134.9, 131.0, 126.0 (q, J = 3.7 Hz), 123.6 (q, J = 27.1 Hz), 26.3; MS (EI, 70 eV) m/z 216 (M<sup>+</sup>, 1), 173 (100), 145 (73), 95 (24), 43 (92).

1-(4-Cyanophenyl)propane-1,2-dione (**2f**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.13 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 7.6 Hz, 2 H), 2.53 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  199.0, 188.9, 135.3, 132.7, 131.0, 117.9, 117.7, 26.2; MS (EI, 70 eV) *m*/*z* 173 (M<sup>+</sup>, 1), 130 (100), 102 (64), 75 (18), 43 (49).

1-*p*-Tolylpropane-1,2-dione (**2g**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ 7.88 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 2.48 (s, 3 H), 2.41 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  201.1, 191.4, 146.1, 130.6, 129.8, 129.4, 26.6, 22.1; MS (EI, 70 eV) *m*/*z* 162 (M<sup>+</sup>, 1), 119 (100), 91 (82), 65 (37).

1-(4-tert-Butylphenyl)propane-1,2-dione (**2h**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.93 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 2.49 (s, 3 H), 1.33 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  201.1, 191.4, 158.9, 130.5, 129.4, 126.1, 35.5, 31.2, 26.6; MS (EI, 70 eV) *m*/*z* 204 (M<sup>+</sup>, 1), 161 (100), 146 (18), 118 (23).

1-(3-Chlorophenyl)propane-1,2-dione (**2i**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.87–7.98 (m, 2 H), 739–7.58 (m, 2 H), 2.50 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 199.7, 189.6, 135.3, 134.6, 133.6, 130.4, 130.3, 128.7, 26.4; MS (EI, 70 eV) m/z 182 (M<sup>+</sup>, 1), 139 (72), 111 (100), 75 (68). Anal. Calcd for C<sub>9</sub>H<sub>7</sub>ClO<sub>2</sub>: C, 59.20; H, 3.86. Found: C, 59.31; H, 3.79.

 $\label{eq:1.2.2.1} \begin{array}{l} 1-(2-Chlorophenyl)propane-1,2-dione~(\textbf{2j}): \ ^{1}H~NMR~(CDCl_{3},~400~MHz)~\delta~7.35-7.40~(m, 2~H),~746-7.48~(m, 1~H),~7.62-7.64~(m, 1~H),~2.55~(s, 3~H); \ ^{13}C~NMR~(CDCl_{3},~100~MHz)~\delta~198.7,~193.2,~134.1,~134.0,~133.3,~131.5,~130.2,~127.5,~25.1;~MS~(EI,~70~eV)~m/z~182~(M^+,~1),~139~(100),~111~(65),~75~(53),~43~(69).~Anal.~Calcd~for~C_9H_7ClO_2:~C,~59.20;~H,~3.86.~Found:~C,~59.33;~H,~3.78. \end{array}$ 

1-(Naphthalen-3-yl)propane-1,2-dione (**2k**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.54 (s, 1 H), 8.01 (d, *J* = 8.8 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 2.56 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  200.9, 191.5, 136.3, 133.4, 132.4, 130.1, 129.6, 129.0, 128.0, 127.2, 124.4, 26.7; MS (EI, 70 eV) *m*/*z* 198 (M<sup>+</sup>, 3), 155 (76), 127 (100), 77 (14), 43 (35).

1–1'-Biphenyl-4-ylpropane-1,2-dione (**2l**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.08 (d, J = 8.4 Hz, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.61 (d, J = 7.6 Hz, 2 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.40 (t, J = 7.2 Hz, 1 H), 2.54 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 200.8, 191.0, 147.3, 139.6, 131.1, 130.6, 129.2, 128.7, 127.6, 127.5, 26.6; MS (EI, 70 eV) m/z 224 (M<sup>+</sup>, 1), 181 (100), 152 (58), 76 (23), 43 (42). Anal. Calcd for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>: C, 80.34; H, 5.39. Found: C, 80.45; H, 5.33.

1-Phenylbutane-1,2-dione (**2m**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.96 (d, J = 7.6 Hz, 2 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 2.89 (t, J = 7.2 Hz, 2 H), 1.18 (t, J = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 204.0, 192.8, 134.8, 132.2, 130.3, 129.1, 32.3, 7.0; MS (EI, 70 eV) m/z 162 (M<sup>+</sup>, 1), 105 (100), 77 (73), 51 (34).

1-Phenylpentane-1,2-dione (**2n**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ 7.96 (d, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 2.84 (t, *J* = 7.2 Hz, 2 H), 1.67–1.77 (m, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  203.6, 192.8, 134.8, 132.2, 130.4, 129.1, 40.9, 16.7, 13.9; MS (EI, 70 eV) *m*/*z* 176 (M<sup>+</sup>, 1), 105 (100), 77 (58), 51 (27).

3-Methyl-1-phenylbutane-1,2-dione (**120**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.91 (d, *J* = 7.6 Hz, 2 H), 7.44–7.62 (m, 3 H), 3.33 (q, *J* = 6.8 Hz, 1 H), 1.18 (q, *J* = 6.8 Hz, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  206.8, 194.3, 134.8, 132.8, 130.1, 129.1, 128.8, 128.5, 36.7, 17.1; MS (EI, 70 eV) *m*/*z* 176 (M<sup>+</sup>, 1), 105 (100), 77 (93), 51 (69), 43 (94).

1-Phenylhexane-1,2-dione (**2p**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.95 (d, *J* = 7.6 Hz, 2 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 2.86 (t, *J* = 7.2 Hz, 2 H), 1.63–1.70 (m, 2 H), 1.34–1.41 (m, 2 H), 0.92 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  203.5, 192.6, 134.6, 132.0, 130.2, 128.9, 38.5, 24.9, 22.3, 13.8; MS (EI, 70 eV) *m*/*z* 190 (M<sup>+</sup>, 1), 105 (100), 77 (74), 57 (48).

#### ASSOCIATED CONTENT

**Supporting Information.** Full experimental details and copies of NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

**Corresponding Author** \*E-mail: jianghf@scut.edu.cn.

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