### Palladium(0)-Catalyzed Reaction of Cyclopropylidenecycloalkanes with Carbon Dioxide

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Cyclopropylidenecycloalkanes, which are highly strained methylenecyclopropane (MCPs) containing a cycloalkane moiety, react with carbon dioxide smoothly to give the corresponding five-membered lactone derivatives in moderate to good yields through a cyclopropane ring-opening process in

### Introduction

Methylenecyclopropanes (MCPs), as highly strained but readily accessible molecules, can undergo a variety of ringopening reactions in the presence of transition metals or Lewis acids because the relief of ring strain can provide a potent thermodynamic driving force.<sup>[1,2]</sup> However, it should also be noted that release of such strain energy (27 kcal/ mol)<sup>[3]</sup> is not sufficient for high reactivity. The  $\pi$  character of the ring bonds of a cyclopropane provides the kinetic opportunity to initiate the unleashing of the strain.<sup>[4]</sup> It is well-known that cyclopropane-containing compounds such as MCPs can easily undergo ring-opening reactions with other substrates in the presence of various transition metal catalysts, giving efficient access to enhanced molecular complexity in organic syntheses.<sup>[5]</sup> More recently, we have also reported that (cyclopropylidenecyclohexyl)benzene derivatives can undergo interesting dehydrogenative rearrangement along with the cyclopropane ring opening process in the presence of AuPPh<sub>3</sub>Cl/AgOTf or Pd(OAc)<sub>2</sub> at high temperature in toluene to give the corresponding biaryl or isopropenylbiaryl derivatives in moderate to good yields.<sup>[6]</sup> These interesting findings have encouraged us to continue to discover more useful transformations with these special MCPs.

Recently, much attention has been focused on the fixation of carbon dioxide because CO<sub>2</sub>, the earth's most abundant carbon resource, is remarkably little used as a chemical feedstock.<sup>[7]</sup> In this area, catalytic fixation of CO<sub>2</sub> into organic compounds using transition metal catalysts to form a new C-C bond from the incorporation of highly strained

the presence of  $Pd^0$  catalyst and  $PCy_3$  upon heating under 40 atm of  $CO_2$ . The relative configuration of the major diastereomers has been determined and a plausible reaction mechanism has also been proposed.

small rings with  $CO_2$  is an important subject. For example, Inoue and co-workers have disclosed that two kinds of lactones could be formed from the reaction of simple MCPs with carbon dioxide (40 atm) upon heating in the presence of palladium(0) complex, affording the corresponding products in 6-77% total yields (Scheme 1).<sup>[8]</sup> As part of our studies on the catalytic fixation of CO<sub>2</sub> by transition metal complexes, we attempted to use these cyclopropylidenecycloalkanes as substrates to investigate their reactions with CO<sub>2</sub> catalyzed by palladium(0) complexes because these methylenecyclopropane derivatives are more strained than simple MCPs, providing an additional driving force to incorporate CO<sub>2</sub>, which is an extremely inert and unreactive gas.



Scheme 1. Palladium-catalyzed reactions of MCPs with CO<sub>2</sub>.

### **Results and Discussion**

Initial studies using (cyclopropylidenecyclohexyl)benzene (1a) as the substrate were aimed at determining the optimal reaction conditions for the palladium(0)-catalyzed reactions; the results of these experiments are summarized in the Supporting Information (Table SI-1). On the basis of the examination of palladium sources, solvents, additives, and phosphane ligands, we found that utilizing 0.2 equiv. of [Pd<sub>2</sub>(dba)<sub>3</sub>] as the catalyst, 0.2 mL of dimethyl sulfoxide (DMSO) as the additive, and  $PCy_3$  as the ligand (0.8 equiv.) at 120 °C in toluene for 36 h, provided 2a and 2'a as a pair of diastereoisomers (5:1) in 76% yield, which served as the best conditions for this transformation (Scheme 2).



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Scheme 2. Optimal reaction conditions for the  $Pd^0$ -catalyzed reaction of 1a with  $CO_2$ .

Having identified the optimized reaction conditions, we next carried out palladium(0)-catalyzed lactonization reactions of a variety of MCPs 1 with CO<sub>2</sub> to evaluate the scope of this reaction. The results are summarized in Table 1. For substrates 1b-g (R<sup>1</sup> = aryl, R<sup>2</sup> = R<sup>3</sup> = H, and n = 1), the corresponding products, 2b-g (and 2'b, 2'g), could be obtained in moderate yields along with moderate diastereomeric ratios (Table 1, entries 1–6). For MCPs 1h-k (R<sup>2</sup> = aryl, R<sup>1</sup> = R<sup>3</sup> = H and n = 1), the reaction also proceeded efficiently to give the corresponding lactone derivatives 2h-k (and 2'h, 2'k) in good yields (74–91%) and moderate diastereomeric ratios (Table 1, entries 7–10). In the case of MCP 1I (R<sup>3</sup> = aryl, R<sup>1</sup> = R<sup>2</sup> = H and n = 1),

Table 1. Reaction of 1 under the optimal conditions with  $CO_2$ .



Entry <sup>[a]</sup>	n	$1 (R^{1}/R^{2}/R^{3})$	Yield (%) <sup>[0]</sup>
			2+2' (2:2')
1	1	<b>1b</b> (C <sub>6</sub> H <sub>5</sub> /H/H)	<b>2b+2'b</b> , 73 (4:1)
2	1	1c ( <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> /H/H)	<b>2c+2'c</b> , 72 (2:1) <sup>[c]</sup>
3	1	1d (o-MeC <sub>6</sub> H <sub>4</sub> /H/H)	<b>2d+2'd</b> , 76 (2:1) <sup>[c]</sup>
4	1	1e ( <i>o</i> , <i>p</i> -Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> /H/H)	<b>2e+2'e</b> , 69 (5:1) <sup>[c]</sup>
5	1	$1f(m,m-Me_2C_6H_3/H/H)$	2f+2'f, 74 (1:1)
6	1	$1g(p-PhC_6H_4/H/H)$	2g+2'g, 65 (3:1)
7	1	<b>1h</b> (H/C <sub>6</sub> H <sub>5</sub> /H)	2h+2'h, 91 (2:1)
8	1	1i (H/p-MeC <sub>6</sub> H <sub>4</sub> /H)	<b>2i+2'i</b> , 88 (3:1) <sup>[c]</sup>
9	1	1j (H/o-MeC <sub>6</sub> H <sub>4</sub> /H)	<b>2j+2'j</b> , 90 (4:3) <sup>[c]</sup>
10	1	1k (H/p-PhC <sub>6</sub> H <sub>4</sub> /H)	2 <b>k</b> +2' <b>k</b> , 74 (4:1) <sup>[c]</sup>
11	1	$11 (H/H/C_6H_5)$	<b>2l+2'l</b> , 86 (5:1) <sup>[c]</sup>
12	0	$1m (H/C_6H_5/H)$	<b>2m+2'm</b> , 85 (1:1) <sup>[c]</sup>
13	2	1n (C <sub>6</sub> H <sub>5</sub> /H/H)	<b>2n+2'n</b> , 74 (4:1) <sup>[c]</sup>
14	1	10 (H/C <sub>4</sub> H <sub>9</sub> /H)	<b>20+2'0</b> , 76 (3:1) <sup>[c]</sup>
15	0	$1p(H/C_4H_9/H)$	<b>2p+2'p</b> , 71 (1:1) <sup>[c]</sup>

[a] Reaction conditions: 1 (0.2 mmol),  $Pd_2(dba)_3$  (0.04 mmol),  $PCy_3$  (0.16 mmol), DMSO (0.2 mL), toluene (2.0 mL), and the reactions were carried out at 120 °C. [b] Isolated yield. [c] The ratios were determined by <sup>1</sup>H NMR spectroscopic data.

the desired product 2l (and 2'l) could also be obtained in 85% yield (Table 1, entry 11).

Changing the cyclohexyl group to a cyclopentyl or cycloheptyl group afforded the corresponding products **2m** (and **2'm**) and **2n** (and **2'n**) in 85 and 74% yields, respectively, along with moderate diastereomeric ratios under the standard conditions (Table 1, entries 12 and 13). Using aliphatic MCPs **10** and **1q** as substrates ( $\mathbb{R}^2 = \mathbb{C}_4\mathbb{H}_9$ ,  $\mathbb{R}^1 = \mathbb{R}^3$ = H), the desired lactone products **20** (and **2'0**) and **2p** (and **2'p**) were obtained in moderate yields with 3:1 and 1:1 diastereomeric ratios, indicating the wide substrate generality in this Pd<sup>0</sup>-catalyzed CO<sub>2</sub> fixation process (Table 1, entries 14 and 15).

The diastereomeric ratios of these lactone products were determined by separation with TLC, silica gel column chromatography, and HPLC, or by <sup>1</sup>H NMR spectroscopic analysis. Furthermore, the structures of the major diastereoisomers **2g** and **2h** have been determined by X-ray diffraction of their single-crystals. The ORTEP drawings are shown in Figures 1 and 2 and their CIF data are presented in the Supporting Information.<sup>[9]</sup> As a result of these investigations, the products **2** were identified as the major diastereoisomers in most cases.



Figure 1. ORTEP drawing of 2g.



Figure 2. ORTEP drawing of 2h.

Using (cyclopropylidenecyclobutyl)benzene (1q) as substrate afforded the expected product 2s in very low yield





Scheme 3. Reaction of MCP 1q with CO<sub>2</sub> under the standard conditions.



Scheme 4. Reactions of 1r and 1s with CO<sub>2</sub> under the standard conditions.

To shed some light on the stereoselectivity of this palladium(0)-catalyzed reaction, density functional theory (DFT) studies have been performed to investigate the conformers of the substrate **1b**.<sup>[10]</sup> The calculation results showed that the relative energy of conformer **P-1**, in which phenyl group is on the equatorial bond, is 17.82 kJ/mol lower than that of conformer **P-2**, in which the phenyl group is on the axial bond (Scheme 5), indicating that conformer **P-1** is more stable.



Scheme 5. Reaction of 1r and 1s with CO<sub>2</sub>.

Based on a series of stabilization investigations on the substrates, a proposed reaction pathway is shown in Scheme 6. Under the standard reaction conditions, the substrate exists predominantly as conformer P-1, which reacts with palladium(0) catalyst to generate intermediate A.<sup>[11]</sup> Intermediate A undergoes a ring-opening process to produce intermediate **B**, in which  $C_a$  position is negatively charged. Therefore, carbon dioxide can approach Ca either from the upside or the underside to produce intermediate **D-1** and intermediate **D-2**, respectively, via intermediate  $\mathbf{C}$ .<sup>[8]</sup> The negatively charged oxygen atom attacks the allyl palladium moiety to produce the corresponding lactones 2 and 2', respectively. The two axial hydrogen atoms (printed in bold) partially impair the incoming CO<sub>2</sub> from approaching from the underside due to steric repulsion, resulting in the formation of lactones 2 as the major diastereomers in most cases. Moreover, according to the previously reported



Scheme 6. A proposed mechanism.

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mechanism in the Pd<sup>0</sup>-catalyzed reaction of simple MCPs with  $CO_2$ ,<sup>[8]</sup> intermediate **C** can also be transformed into intermediate **E**, producing the other two regioisomers **3** and **3**' through intermediates **F-1** and **F-2**, respectively. However, the cycloalkanes bearing an aromatic group in cyclo-propylidenecycloalkanes **1** sterically favor the formation of intermediate **C** and disfavor the formation of intermediate **E** at high temperature, therefore affording products **2** and **2**' exclusively. This expains why only regioisomers **2** and **2**' were exclusively formed in the above catalytic system.

Under the standard conditions, we succeeded in the synthesis of ( $\pm$ )-norbakkenolide A from MCP 3.<sup>[12]</sup> As shown in Scheme 7, this interesting biologically active compound,<sup>[13]</sup> which, for instance, shows cytotoxic and antifeedant activities, inhibition of the activity against platelet activation factor, and activity as an antiplatelet aggregatory agent, was obtained in 50% yield as a pair of diastereoisomers (major/minor = 1:0.85) under the standard conditions.



Scheme 7. Reactions of MCP 3 with  $CO_2$  under the standard conditions.

In conclusion, we have developed an interesting  $Pd^0$ -catalyzed transformation of cyclopropylidenecycloalkanes with carbon dioxide, giving the corresponding five-membered lactone derivatives in moderate to good yields (up to 91%) along with high regioselectivities. Because lactones constitute core structural units for a wide range of functional molecules and are synthesized primarily using several steps from ketones,<sup>[14]</sup> this palladium-catalyzed process provides an alternative way to attain such compounds easily. Interestingly, this reaction displays moderate diastereoselectivity with respect to a series of substrates; the relative configuration of the major products was established by X-ray diffraction analysis. Efforts are in progress to further understand the scope and limitations of this reaction.

### **Experimental Section**

**General Remarks:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AM-300 spectrometer for solutions in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard; *J* values are given in Hz. Mass spectra were recorded by EI methods, and HRMS were measured with a Finnigan MA<sup>+</sup> mass spectrometer. The employed solvents were dried by standard procedures. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

**General Procedure:** A dried tube equipped with a magnetic stirring bar was charged with MCP (0.2 mmol),  $[Pd_2(dba)_3]$  (0.04 mmol),  $PCy_3$  (0.16 mmol), anhydrous toluene (2.0 mL), and anhydrous DMSO (0.2 mL), and then CO<sub>2</sub> was bubbled through for 2 min.

The tube was placed in an autoclave and the pressure was raised to 40 atm with a  $CO_2$  cylinder after purging the autoclave with  $CO_2$  three times. The reaction was heated to 110–120 °C (oil bath). After 36 h, the reaction was stopped and the pressure was reduced to 1 atm. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO<sub>2</sub>) to give the corresponding products **2** and **2**'.

**Supporting Information** (see footnote on the first page of this article): Detailed description of experimental procedures, the CIF data of **2g** and **2h**, full characterization of new compounds.

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