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# Platinum-on-Carbon-Catalyzed Aqueous Oxidative Lactonization of Diols by Using Molecular Oxygen

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**Abstract** A lactonization of various diols catalyzed by platinum on carbon (Pt/C) in water under an atmosphere of molecular oxygen was developed. Derivatives of 1,4- 1,5- and 1,6-diols were transformed into the corresponding five-, six-, and seven-membered lactones by the present oxidative lactonization method.

Key words lactones, diols, lactonization, platinum catalysis, water, green chemistry

Lactones are important frameworks in the organic, pharmaceutical, and industrial fields. Various synthetic methods have been developed for the construction of lactone skeletons, including intramolecular hydroacyloxylation of olefinic acids,<sup>1</sup> intramolecular esterification of hydroxy acids,<sup>2</sup> and Baeyer–Villiger reactions of cyclic ketones.<sup>3</sup> The oxidative lactonization of easily available diol substrates is also useful and has been extensively investigated.<sup>4-15</sup> Stoichiometric metal reagents such as silver<sup>4</sup> or chromium<sup>5</sup> have been traditionally used in the oxidative lactonization of diols. Meanwhile, several catalytic methods that use a transition metal with an oxidant such as oxygen,<sup>6-13</sup> hydrogen peroxide,<sup>14</sup> or a carbonyl compound<sup>15</sup> have been developed, and transition-metal-catalyzed dehydrogenations of diols to give lactones have also been reported.<sup>12,16</sup> Among these, the lactonization of diols under an atmosphere of O<sub>2</sub> as an oxidant is valuable from the viewpoint of atom economy and green sustainability, because the only byproduct is water. Although homogeneous Ru,<sup>6</sup> Pd,<sup>7</sup> or Ir<sup>8</sup> species or heterogeneous Mn,<sup>9</sup> Ru,<sup>10</sup> Pd,<sup>11</sup> Co,<sup>12</sup> or Au<sup>13</sup> species have been reported to catalyze the lactonization of diols under O<sub>2</sub>, the use of an organic solvent was essential in all cases. A transformation using preactivated PtO<sub>2</sub> in acetone-water has also been reported as part of a



total synthesis.<sup>17</sup> We now report the Pt/C-catalyzed clean oxidative lactonization of diols in water under an atmosphere of molecular oxygen.

We have previously reported a dehydrogenative oxidation of primary alcohols to carboxylic acids catalyzed by palladium on carbon (Pd/C) in water, which proceeds via the corresponding aldehyde and a subsequent hydrate intermediate.<sup>18</sup> When 1,2-phenylenedimethanol (**1a**), bearing two benzylic alcohol functions, was used as a substrate under Pd/C-catalyzed dehydrogenation conditions in water under an Ar atmosphere at 80 °C for six hours, the desired lactone product, the phthalide 2a, was obtained in a low (10%) yield (Table 1, entry 1). This lactonization of 1a proceeds through oxidation of the primary benzylic alcohol moiety to the corresponding aromatic aldehyde as an intermediate during the first oxidative step (see Scheme 2, below). We therefore performed the reaction of **1a** under an oxygen atmosphere with the aim of quenching the generated hydrogen, which is responsible for the reverse reaction (catalytic hydrogenation of the aromatic aldehyde), with  $O_2$ .<sup>19</sup> As a result, **1a** was transformed into **2a** in moderate yield (entry 2). Encouraged by this result, we examined the effects of various metal-on-carbon catalysts (entries 2-8). Pt/C and Ir/C showed higher catalytic activities, giving 2a in yields of 74 and 75%, respectively (entries 3 and 4), whereas the use of Au/C produced incomplete lactonization to give 2a in 57% yield, together with recovered 1a in 26% yield (entry 5).<sup>20</sup> Rh/C, Ru/C, and Cu/C were ineffective catalysts (entries 6-8), although Ru/C has been reported to be an efficient catalyst for the oxidation of alcohols by oxygen in toluene to give carbonyl compounds.<sup>21</sup> On decreasing the catalyst loading of Ir/C to 1 mol%, the reaction efficiency drastically decreased (entry 9). In contrast, 1 mol% of Pt/C retained sufficient catalytic activity (entry 10), and 2a was obtained in 88% isolated yield on extending the reaction time to 12 hours, even in the presence of only 0.5 mol% of

Pt/C (entry 11). A further decrease in the loading of Pt/C (0.1 mol%) or a lower reaction temperature ( $60 \degree$ C) led to a lower yield of **2a** (entries 12 and 13). The starting material **1a** was not completely consumed under an air atmosphere (entry 14), and the lactonization did not proceed at all under an argon atmosphere (entry 15).

Table 1 C	atalyst Effects
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	ОН	catalyst (X m	nol%), O <sub>2</sub> (balloo	on)		
ОН -		H <sub>2</sub> O (1	I mL), 80 °C			
<b>1a</b> (0	.25 mmol)				2a	
Entry	Catalyst	Mol%	Time (h)	Yieldª (%)		
				1a	2a	
1 <sup>b</sup>	10% Pd/C	10	6	34	10	
2	10% Pd/C	10	6	0	55	
3	10% Pt/C	10	6	0	74	
4	10% lr/C	10	6	0	75	
5	10% Au/C	10	6	26	57	
6	10% Rh/C	10	6	34	15	
7	10% Ru/C	10	6	20	4	
8	10% Cu/C	10	6	78	0	
9	10% lr/C	1	6	33	10	
10	10% Pt/C	1	6	9	81	
11	10% Pt/C	0.5	12	2	90 (88) <sup>c</sup>	
12	10% Pt/C	0.1	12	36	45	
13 <sup>d</sup>	10% Pt/C	0.5	12	26	66	
14 <sup>e</sup>	10% Pt/C	0.5	12	56	30	
15 <sup>b</sup>	10% Pt/C	0.5	12	82	0	

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy with 1,3-benzodioxole (30.5 mg, 0.25 mmol) as an internal standard.

<sup>b</sup> Under argon

<sup>c</sup> Isolated yield

<sup>d</sup> The reaction was carried out at 60 °C.

<sup>e</sup> Under air.

 Table 2
 Pt/C-catalyzed oxidative lactonization of diols.

		HO OH 10% Pt/C (0.5 mol%), O <sub>2</sub> H <sub>2</sub> O (1 mL), 80	2 (balloon) °C, 12 h	
Entry	Substrate	product		Yield <sup>a</sup> (%)
1	R = H (1a)	R C C C C C C C C C C C C C C C C C C C	R C C C C C C C C C C C C C C C C C C C	88 (82) <sup>b</sup>
2	R = Me ( <b>1b</b> )	2ba	2bb	82 (32:68) <sup>c</sup>
3	R = Br ( <b>1c</b> )	2ca	2cb	26 (12:88) <sup>c</sup>
4	R = F ( <b>1d</b> )	2da	2db	89 (29:71) <sup>c</sup>

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The scope of the substrates was next examined in the presence of Pt/C (0.5 mol%) in water under an O<sub>2</sub> atmosphere at 80 °C for 12 hours (Table 2). A 5 mmol (0.69 g)scale reaction with **1a** as a substrate was successfully performed to give 2a in 82% yield (Table 2, entry 1). 1,2-Phenylenedimethanol derivatives 1b-d bearing various substituents at the 4-position of their aromatic nuclei were smoothly transformed into the corresponding phthalide derivatives **2b-d** as isomeric mixtures (entries 2-4). In these reactions, the 5-substituted phthalides 2ba-da were obtained as the major products.<sup>22</sup> The reactions of 4,5-dimethoxy-1.2-phenylenedimethanol (1e) and of 4.5-dichloro-1,2-phenylenedimethanol (1f) proceeded similarly to give the corresponding lactones 2e and 2f, together with residual starting material and/or a dialdehvde as a byproduct, as confirmed by <sup>1</sup>H NMR analysis (entries 5 and 6). Substrate **1g**, bearing both primary and secondary alcohol moieties within the molecule, was also converted into the desired lactone product **2g** in moderate yield (entry 7). The reaction of the unsymmetrical diol 1h gave a mixture of 1-isochromanone (**2ha**) and 3-isochromanone (**2hb**) (entry 8): preferential oxidation of the benzylic alcohol moiety provided 2ha as the major isomer. 1,8-Bis(hydroxymethyl)naphthalene (1i) was smoothly converted into the 1,8-naphthalide 2i (entry 9). The present method was also applicable to the synthesis of the seven-membered-ring lactone 2j from 2,2'bis(hydroxymethyl)-1,1'-biphenyl (1j), albeit in low yield (entry 10). The yield of 2j was not improved by raising the temperature to 120 °C or increasing the O<sub>2</sub> pressure to 3 atm. The lactonization of 2-phenylbutane-1,4-diol (1k) afforded an 88:12 mixture of isomers 2ka and 2kb in good yield (entry 11). Butane-1,4-diol (11), as a simple linear aliphatic diol, was transformed into  $\gamma$ -butyrolactone (21) in only 19% yield, with the formation of the acyclic dicarboxylic acid **31** as an undesired byproduct (entry 12), whereas the reaction of *cis*-di(hvdroxymethyl)cvclohexane (**1m**), as an alicyclic diol, provided the corresponding lactone 2m in moderate yield (entry 13).

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## Table 2 (continued)

Entry	Substrate	product		Yield <sup>a</sup> (%)
5	MeO MeO 1e	MeO MeO 2e		43
6	CI OH CI OH			40 (21) <sup>d</sup>
7 <sup>e</sup>	OH OH 1g	2g		56 (20) <sup>d</sup>
8 <sup>e</sup>	OH OH	O D Dha	C C C C C C C C C C C C C C C C C C C	50 (72:28) <sup>c</sup> (10) <sup>d</sup>
9 <sup>e</sup>	HO HO 1i			70 (24) <sup>d</sup>
10 <sup>e</sup>				21 (15) <sup>f</sup> (29) <sup>g</sup>
11 <sup>e</sup>	OH OH 1k	2ka		78 (88:12) <sup>c</sup> (5) <sup>d</sup>
12 <sup>h</sup>	HO 1I	21	CO <sub>2</sub> H CO <sub>2</sub> H 3I	<b>2I</b> : 25 <sup>i</sup> <b>3I</b> : 19
13	H H H Im	H H 2m		47

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<sup>a</sup> Isolated yield.
<sup>b</sup> 5 mmol scale.
<sup>c</sup> The ratio of the two isomers was determined by <sup>1</sup>H NMR spectroscopy of the crude product.
<sup>d</sup> Recovered starting material.
<sup>e</sup> The reaction was stirred for 24 h.
<sup>f</sup> At 120 °C.
<sup>g</sup> Under 3 atm O<sub>2</sub> pressure.
<sup>h</sup> Succinic acid was obtained in 19% yield.
<sup>i</sup> The yield was determined by <sup>1</sup>H NMR using 1,3-benzodioxole as an internal standard.

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When the benzyl alcohol derivative **4** was used as a substrate instead of the diol **1**, a mixture of 4-methylbenzaldehyde (**5**) and 4-methylbenzoic acid (**6**) was obtained, even after 12 hours (Scheme 1, Equation 1). In addition, 2-(hydroxymethyl)benzoic acid (**7**) was converted into the phthalide **2a** in both the presence and absence of Pt/C (Scheme 1, Equation 2). The present reaction could also be carried out in various organic solvents [DMF, cyclopentyl methyl ether (CPME), or toluene] instead of water, giving **2a** in good yields (Scheme 1, Equation 3).



Two plausible reaction pathways for lactonization of the diols are conceivable, as shown in Scheme 2. Dehydrogenation<sup>18</sup> of **1a** first gives the hydroxy aldehyde **A**. O<sub>2</sub> can quench the generated H<sub>2</sub> in the presence of Pt/C to generate H<sub>2</sub>O<sub>2</sub>, which is nearly instantaneously degraded to H<sub>2</sub>O and O<sub>2</sub>.<sup>19</sup> The direct oxygen oxidation<sup>23</sup> of **1a** to **A** is also possible. The desired lactone **2a** is constructed through hemiacetal formation between the benzyl alcohol and aromatic aldehyde functionalities to give **B**, and a subsequent dehydrogenative or oxygen oxidation process (path A). Alternatively,

hydration of the aldehyde moiety in **A** gives intermediate **C**, which undergoes oxidation to produce the hydroxy acid intermediate **D**. Subsequent intramolecular condensation of **D** produces **2a** (path B). Whereas the lactonization in organic solvents (Scheme 1, Equation 3) proceeds by path A without the formation of hydrate **C**, the lactonization in water can proceed by both pathways A and B, as demonstrated in Scheme 1, Equations 1 and 2.

We have accomplished an oxidative lactonization of a variety of diols by using  $Pt/C^{24}$  as a catalyst in aqueous medium under an oxygen atmosphere. The present catalytic method in environmentally benign water, with molecular oxygen as a clean oxidant (hydrogen acceptor), is valuable from the viewpoint of green sustainability and atom efficiency. Furthermore, the use of water is advantageous as it suppresses the potential ignition properties of Pt/C.

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#### Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611917.

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- (20) 2-Benzofuran-1(3H)-one (2a); Typical Procedure

A test tube was charged with 1,2-phenylenedimethanol (1a; 34.5 mg, 0.25 mmol), 10% Pt/C (2.5 mg, 0.00125 mmol, 0.5 mol%), and H<sub>2</sub>O (1 mL), then sealed with a septum. The atmosphere in the test tube was replaced with O<sub>2</sub> (balloon), and the mixture was stirred with a ChemiStation (EYELA Tokyo Rikakikai Co., Ltd., Tokyo, Japan) and heated at 80 °C for 12 h. The mixture was then cooled to r.t. and passed through a membrane filter (Millex-LH 0.20  $\mu$ m; Millipore) to remove the insoluble catalyst. The filtrate was extracted with EtOAc (3 × 5.0 mL), and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–EtOAc) to give a white solid; yield: 29.5 mg (0.22 mmol, 88%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.93 (d, J = 7.5 Hz, 1 H), 7.70 (t, J = 7.5 Hz, 1 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.52 (d, J = 7.5 Hz, 1 H), 5.34 (s, 2 H).

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- (24) Analysis by atomic absorption spectrometry indicated that no Pt metal (<1 ppm) leached into the reaction mixture during the first run (Table 1, entry 11). When recovered Pt/C was used in a second run, **2a** was obtained in 77% yield together with the starting material **1a** (11% yield).