#### Letter

# Ruthenium-Catalyzed Oxidative Dearomatization of Indoles for the Construction of C2-Quaternary Indolin-3-ones

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**Abstract** A ruthenium-catalyzed oxidative dearomatization of 2-alkylor 2-aryl-substituted indoles has been developed. When coupled with a cascade transformation, it provides a new system for the construction of indolin-3-ones bearing a C2-quaternary functionality. The reaction occurs readily with RuCl<sub>3</sub>·3H<sub>2</sub>O as a catalyst in acetonitrile. 2-(3-Indolyl)substituted indolin-3-ones were obtained in medium to high yields. A mechanism for the reaction is also proposed.

Key words ruthenium catalysis, oxidation, dearomatization, indoles, indolinones

The oxidation process has been widely recognized as a powerful strategy for the synthesis of cyclic or heterocyclic oxo compounds from the corresponding substrates. However, little effort has been devoted to the oxidation of aromatic or heteroaromatic compounds. Amongst the heteroaromatic systems, indoles are by far the most widely exploited.<sup>1</sup> They are easily derivatized by nucleophilic addition or Friedel–Crafts reactions, so they have a great value in the preparation of natural products, pharmaceuticals, and other fine chemicals.<sup>2</sup>

In the past, molybdenum pentoxide,<sup>3</sup> *m*-chloroperoxybenzoic acid (MCPBA),<sup>4</sup> DDQ,<sup>5</sup> and dimethyldioxirane<sup>6</sup> have been used in rapid oxidations of indoles to oxoindolines as the primary methods for synthesizing these compounds (Figure 1). However, these processes have many limitations, such as toxic metal pollution, incompatibility with many functional groups, low yields, and poor selectivity. Fortunately, a few methods for transition metal catalyzed oxidations of indoles have been reported. An efficient and highly selective ruthenium-porphyrin catalyzed oxidation of *N*-tosylindoles<sup>7</sup> to give 3-oxoindolines was achieved by Che and co-workers using 2,6-dichloropyridine *N*-oxide as the oxidant (Figure 1). Recently, a palladium-catalyzed oxidative dearomatization of indoles has been reported by Guchhait et al.<sup>8a</sup> for the synthesis of C2-quaternary indolin-3ones. However, *tert*-butyl hydroperoxide (TBHP, 2.2 equiv) and  $MnO_2$  (2.0 equiv) were employed in excess as oxidants (Figure 1). At the same time, we achieved a palladium-catalyzed Wacker-type oxidation, oxidation–hydroxylation, and oxidation–methoxylation of *N*-Boc-protected indoles for the preparation of 3-oxoindolines.<sup>9</sup> Although many methods have been developed for the synthesis of 3-indolin-3ones skeletons,<sup>8b-e</sup> transition metal catalyzed systems to realize the direct oxidation of indoles deserve more attention.



Figure 1 Systems for the oxidation of indoles to give 3-oxoindolines

Ruthenium catalysts<sup>10</sup> have played an important role in the recent development of catalytic oxidation reactions. Ruthenium-catalyzed oxidations of alkanes,<sup>11</sup> alcohols,<sup>12</sup> and ethers<sup>13</sup> are typical methods for the synthesis of carbonyl compounds. Other oxidative transformations, such as

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ruthenium-catalyzed asymmetric epoxidations of alkenes,<sup>14</sup> cleavage of double bonds,<sup>15</sup> and biomimetic oxidations of amines<sup>16</sup> and phenols<sup>17</sup> under mild conditions also play an important role in transition metal catalyzed oxidations of organic compounds. Therefore, ruthenium-catalyzed oxidations of heteroaryl compounds, especially indoles, should clearly provide a variety of practical and useful methods for the preparation of heterocyclic oxo compounds. In addition, sodium periodate (NaIO<sub>4</sub>) has been extensively used in ruthenium-catalyzed oxidations of alkenes,<sup>18</sup> amides,<sup>19</sup> and alcohols,<sup>20</sup> representing, therefore, a potentially interesting oxidant agent in the oxidative dearomatization of indoles. Here, we report a ruthenium-catalyzed oxidative dearomatization of indoles in the presence of NaIO<sub>4</sub> (Scheme 1).



In the course of our research on ruthenium-catalyzed oxidative dearomatization of indoles, we obtained 2-indolyl-3-oxoindoline as a main product. Our initial experiment began with 2-phenylindole (**1a**) as a model starting material,  $NalO_4$  (1.5 equiv) as an oxidant, and ruthenium trichloride

Table 1 0	ptimization of the Conditions fo	r Ruthenium-Catalyzed Oxidative Dearon	natization of 2-Phenylind	ole ( <b>1a</b> )ª					
$ \begin{array}{cccc} & & & \\ & & & & $									
Entry	Catalyst (mol%)	Oxidant (equiv)	Solvent	Temp (°C)	Yield <sup>b</sup> (%)				
1	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.5)	EtOAc	40	36				
2	$RuCl_3 \cdot 3H_2O(5)$	70 wt% aq TBHP	EtOAc	40	15				
3	$RuCl_3 \cdot 3H_2O(5)$	( <sup>t</sup> BuO) <sub>2</sub> (3.0)	EtOAc	40	NR				
4	$RuCl_3 \cdot 3H_2O(5)$	30 wt% aq H <sub>2</sub> O <sub>2</sub> (12.0)	EtOAc	40	trace				
5	$RuCl_3 \cdot 3H_2O(5)$	AcOOH (3.0)	EtOAc	40	trace				
6	$RuCl_3 \cdot 3H_2O(5)$	O <sub>2</sub> (1 atm)	EtOAc	40	NR				
7	$RuCl_3 \cdot 3H_2O(5)$	NaIO <sub>4</sub> (1.5)	THF	40	trace				
8	$RuCl_3 \cdot 3H_2O(5)$	NaIO <sub>4</sub> (1.5)	acetone	40	57				
9	$RuCl_3 \cdot 3H_2O(5)$	NaIO <sub>4</sub> (1.5)	MeCN	40	55				
10	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.5)	acetone	60	63				
11	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.5)	MeCN	60	75				
12	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.5)	MeCN	70	88				
13	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.5)	MeCN	80	86				
14	$RuCl_2(PPh_3)_3(5)$	NalO <sub>4</sub> (1.5)	MeCN	70	55				
15	Ru(acac) <sub>3</sub> (5)	NalO <sub>4</sub> (1.5)	MeCN	70	trace				
16	[RuCl <sub>2</sub> ( <i>p</i> -cymene)] <sub>2</sub> (5)	NalO <sub>4</sub> (1.5)	MeCN	70	59				
17	FeCl <sub>3</sub> (10)	NalO <sub>4</sub> (1.5)	MeCN	70	41				
18	$Fe(acac)_3$ (10)	NalO <sub>4</sub> (1.5)	MeCN	70	trace				
19	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	NalO <sub>4</sub> (1.5)	MeCN	70	trace				
20	$CuCl_2 \cdot 2H_2O(10)$	NalO <sub>4</sub> (1.5)	MeCN	70	20				
21	-	NalO <sub>4</sub> (1.5)	MeCN	70	trace				
22	$RuCl_3 \cdot 3H_2O(5)$	NalO <sub>4</sub> (1.2)	MeCN	70	92				
23	$RuCl_3 \cdot 3H_2O(5)$	NaIO <sub>4</sub> (1.0)	MeCN	70	97				

<sup>a</sup> Reaction conditions: **1a** (97 mg, 0.50 mmol), catalyst, oxidant, solvent (3.0 mL), 24 h.

<sup>b</sup> Isolated yield.

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 $(\text{RuCl}_3 \cdot 3\text{H}_2\text{O})$  as a catalyst in ethyl acetate (EtOAc). The required product, 2-phenyl-2-(2-phenyl-1*H*-indol-3-yl)indolin-3-one (**2a**), was isolated, but only in 36% yield (Table 1, entry 1). This result encouraged us to adhere to our initial hypothesis that a ruthenium catalyst might be a suitable catalyst in the oxidative dearomatization of indoles. We therefore evaluated other oxidants, solvents, and catalysts with the aim of improving the yield of indolinone **2a**.

First, we tested *tert*-butyl hydroperoxide (TBHP; Table 1, entry 2), di-tert-butyl peroxide [('BuO)<sub>2</sub>, entry 3], H<sub>2</sub>O<sub>2</sub> (entry 4), peracetic acid (AcOOH, entry 5), and oxygen  $(O_2, en$ try 6) as oxidants in an attempt to improve the yield of **2a**. The results showed that NaIO<sub>4</sub> is the best oxidant for the ruthenium-catalyzed oxidative dearomatization of indoles, although it gave relatively low yields. A 15% yield of **2a** was obtained when TBHP was chosen as the oxidant, and the other oxidant showed no oxidative activity in the ruthenium-catalyzed oxidative dearomatization of **1a**. When H<sub>2</sub>O<sub>2</sub> or AcOOH was chosen as the oxidant, many bubbles escaped from the solvent surface, possibly as a result of the decomposition of these oxidants in the presence of the ruthenium salt. Tetrahydrofuran (THF, entry 7), acetone (entry 8), and acetonitrile (entry 9) were then evaluated as solvents in the presence of NaIO<sub>4</sub> (1.5 equiv) at 40  $^{\circ}$ C in an attempt improve the yield of the product 2a. The reaction was completely inhibited when THF was used as a solvent in the presence of RuCl<sub>3</sub>·3H<sub>2</sub>O, and the yield improved to 57% and 55% when acetone or acetonitrile, respectively, was used as the solvent. Next, the temperature was increased in an attempt to improve the yield of 2a in acetone and acetonitrile. An 88% yield was obtained when the reaction was carried out at 70 °C in acetonitrile (entry 12). Higher temperatures did not improve this result (entry 13; 80 °C, 86%). To test the activity of other catalysts, several metal salts were evaluated.  $RuCl_2(PPh_3)_3$  (entry 14),  $Ru(acac)_3$  (entry 15), [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (entry 16), FeCl<sub>3</sub> (entry 17), Fe(acac)<sub>3</sub> (entry 18), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (entry 19), and  $CuCl_2 \cdot 2H_2O$  (entry 20), when tested in the presence of NaIO<sub>4</sub> (1.5 equiv) in MeCN at 70 °C failed to give better results, suggesting that RuCl<sub>3</sub>·3H<sub>2</sub>O might be the most effective catalyst. Finally, the amount of NaIO<sub>4</sub> was examined, and a 97% yield of **2a** was obtained when  $NaIO_4$  (1.0 equiv) was used as the oxidant (entry 23). By the optimization of oxidant, solvent and catalyst, the best reaction conditions were identified as RuCl<sub>3</sub>·3H<sub>2</sub>O (5.0 mol%) as catalyst with NaIO<sub>4</sub> (1.0 equiv) as the oxidant in MeCN at 70 °C.

Having identified the optimal conditions, we examined the substrate scope by subjecting a variety of indoles **1a–n** to the ruthenium-catalyzed oxidative dearomatization (Table 2). Indoles **1a–d** with 2-aryl groups gave moderate to high isolated yields (75–97%) of products **2a–d**, respectively (Table 2, entries 1–4). Products **2e–h** were obtained in 67– 85% yield from the ruthenium-catalyzed oxidative dearomatization reactions of the 2-methyl substituted indoles **1e–h** (entries 5–8). To extend the scope of the substrates, we also tested *N*-methyl and *N*-ethyl indoles **1i**–**k** under the optimal reaction conditions and we obtained the corresponding products **2i**–**k** in 81–87% yield (entries 9–11). However, in the case of the 2-ethoxycarbonyl indole **1I** (entry 12), no product was detected and the starting material was recovered. Indole (**1m**; entry 13) and *N*-methylindole (**1n**; entry 14), without any substituents on the 2-position, also failed to give the target products, and the reaction systems were complex.

 Table 2
 Ruthenium-Catalyzed Oxidative Dearomatization Reactions of Indoles<sup>a</sup>



-							
1	1a	Ph	Н	Н	2a	97	
2	1b	4-Tol	Н	Н	2b	85	
3	1c	$4-EtC_6H_4$	Н	Н	2c	75	
4	1d	$4-FC_6H_4$	Н	Н	2d	85	
5	1e	Me	Н	Н	2e	85	
6	1f	Me	Н	Me	2f	82	
7	1g	Me	Н	OMe	2g	67	
8	1h	Me	Н	Cl	2h	79	
9	1i	Ph	Me	Н	2i	87	
10	1j	Ph	Et	Н	2j	82	
11	1k	Me	Me	Н	2k	81	
12	11	CO <sub>2</sub> Et	Н	Н	21	NA	
13	1m	Н	Н	Н	2m	NA	
14	1n	Н	Me	Н	2n	NA	

 $^a$  Reaction conditions: 1 (0.50 mmol), RuCl\_3-3H\_2O (6.5 mg, 0.025 mmol, 5.0 mol%), NaIO\_4 (107 mg, 0.50 mmol, 1.0 equiv), MeCN (3.0 mL), 70 °C, 24 h.  $^b$  Isolated yield.

These results indicated that substrates with 2-aryl or 2-methyl groups react under the optimal conditions, but no target product was detected when a 2-*H* indole was chosen as the substrate. Furthermore, the optimized conditions are also appropriate for the oxidation of *N*-methyl and *N*-ethyl indoles. Note that the catalytic system is not appropriate for a cross-reaction between two different indoles, such as 2-methylindole and 2-phenylindole or 2-methylindole and indole, because of the low selectivity of the C–C bond-formation reaction. This is attributed to the relatively high reactivity of the starting materials and the relatively high oxidative activity of the C–C bond-formation process.

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To investigate the mechanism of the ruthenium-catalyzed oxidative dearomatization of indole **1a**, we introduced TEMPO (1.05 equiv) into the reaction system, and we obtained only a trace amount of the target product **2a** (Scheme 2). Most of the starting material **1a** was recovered. This result indicated that the reaction might proceed by a radical process.



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On the basis of the above results and the known mechanism of the Pd-catalyzed oxidation of indoles<sup>8,9</sup> and the ruthenium-catalyzed oxidation of phenols,<sup>17</sup> a possible mechanism for the ruthenium-catalyzed oxidative dearomatization reaction of indoles is proposed (Figure 2). The activated ruthenium catalyst RuO<sub>4</sub> is formed from ruthenium precursor RuCl<sub>3</sub>·3H<sub>2</sub>O in the presence of NaIO<sub>4</sub>. The activated catalyst RuO<sub>4</sub> reacts with indole **1** to produce the free-radical intermediate **A**, which then forms the complex **B** under the standard reaction conditions. An electron-transfer process gives [RuO<sub>2</sub> + HO<sup>-</sup>] together with the iminium intermediate **C**. This intermediate is trapped by another indole to give the final product **1**. The activated ruthenium catalyst RuO<sub>4</sub> is regenerated in the presence of NaIO<sub>4</sub>.





In summary, by using NaIO<sub>4</sub> as an oxidant, the rutheniumcatalyzed oxidative dearomatization of indoles was successfully achieved, with up to 97% yield.<sup>21</sup> The reactions afforded 2-indolyl-3-oxoindolines with high regioselectivity under the optimal conditions. The principle of these reactions will provide a new strategy for developing new types of ruthenium-catalyzed oxidative dearomatizations of aromatic and heteroaromatic compounds.

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# **Supporting Information**

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- (21) Ruthenium-Catalyzed Oxidative Dearomatization of Indoles 1; General Procedure

A mixture of indole **1** (0.50 mmol), NaIO<sub>4</sub> (107 mg, 0.50 mmol, 1.0 equiv), and RuCl<sub>3</sub>·3H<sub>2</sub>O (6.5 mg, 0.025 mmol, 5.0 mol%) in MeCN (3 mL) was added to a 25 mL Schlenk flask at r.t. and the mixture was then stirred at 70 °C until the reaction was complete. Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography [silica gel, PE–EtOAc (10:1 to 5:1)].

**2,2'-Diphenyl-1,2-dihydro-1'H,3H-2,3'-biindol-3-one (2a)** Yellow solid; yield: 97.0 mg (97%); mp 220–223 °C. IR (neat): 3058, 3025, 2910, 1696, 1618, 1470, 1439, 1074, 1026, 919, 742 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 11.34$  (s, 1 H), 8.33 (s, 1 H), 7.51 (dd, J = 8.3, 7.1 Hz, 1 H), 7.39–7.33 (m, 3 H), 7.25 (d, J = 7.7 Hz, 1 H), 7.16–7.11 (m, 3 H), 7.06–7.01 (m, 6 H), 6.98 (d, J = 8.3 Hz, 1 H), 6.78–6.69 (m, 2 H), 6.61 (d, J = 8.0 Hz, 1 H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ ):  $\delta = 200.5$ , 160.1, 139.8, 138.0, 137.5, 135.8, 133.2, 129.5, 127.6, 127.4, 127.0, 124.4, 121.2, 120.3, 118.7, 118.5, 117.5, 111.9, 111.3, 111.0, 71.2. HRMS (ESI): m/z [M + Na]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>NaO: 423.1473; found: 423.1477.

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