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## RuCl<sub>3</sub>-DCHA Catalyst System: A Selective Aerobic Oxidation of Primary Benzylic Alcohols Under Mild Conditions

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### RuCl<sub>3</sub>-DCHA CATALYST SYSTEM: A SELECTIVE AEROBIC OXIDATION OF PRIMARY BENZYLIC ALCOHOLS UNDER MILD CONDITIONS

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#### **GRAPHICAL ABSTRACT**



**Abstract** The aerobic oxidation of benzylic alcohols to their corresponding aldehydes was performed in a  $RuCl_3 \cdot 3H_2O$ -dicyclohexylamine (DCHA) catalyst system under ambient atmosphere at room temperature. It is noteworthy that the  $RuCl_3 \cdot 3H_2O$ -DCHA system displayed a preference for the primary versus secondary benzylic alcohols in both intermolecular and intramolecular competition experiments.

Keywords Benzylic alcohol; oxidation; RuCl<sub>3</sub> · 3 H<sub>2</sub>O

#### INTRODUCTION

The oxidation of alcohols to the corresponding aldehydes or ketones is an important process in organic synthesis. Many traditional reagents for converting alcohols to carbonyl compounds have been reported over the past years, such as hypochlorite,<sup>[1]</sup> chromium(VI) oxide,<sup>[2]</sup> dichromate,<sup>[3]</sup> manganese(IV) oxide,<sup>[4]</sup> permanganate,<sup>[5]</sup> ruthenium(VII) oxide,<sup>[6]</sup> iodosobenzene,<sup>[7]</sup> and cerium ammonium nitrate (CAN).<sup>[8]</sup> Unfortunately, these hazardous or toxic oxidizing agents often requires usage in stoichiometric amounts leading to the presence of heavy metals in waste. This can cause profoundly harmful effects on the environment. To reduce the damage inflicted on the environment, it is necessary to develop an environmentally friendly process for the oxidation of alcohols. With this aim in mind, many

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metal-catalyzed "green" aerobic oxidations of alcohols to the corresponding carbonyl compounds have been proposed. The benign effects on the environment as well as the potential utility of such reactions are significant advances.<sup>[9]</sup> In recent years, many catalytic methods for aerobic oxidation of alcohols have been reported, displaying a large array of transition-metal catalysts (e.g., Fe, Co, Cu, Au, Ru, Pd, Os).<sup>[10]</sup> The palladium-based catalysts<sup>[11]</sup> and ruthenium compounds<sup>[12]</sup> are particularly useful for this process, but reports of palladium- or ruthenium-catalyzed alcohol oxidations employing oxygen (or air) as the sole oxidant are limited, especially those displaying a preference for the primary versus the secondary hydroxyl group of either an aliphatic or a benzylic diol.<sup>[12d]</sup>

In our research on the oxidation of benzyl alcohol to benzaldehyde, we found an interesting oxidation process based on  $RuCl_3 \cdot 3H_2O$  catalyst. We report herein a simple and general procedure for the aerobic oxidation of benzylic alcohols to the corresponding aldehydes.

In our initial attempts, the oxidation of benzyl alcohol was selected as a model reaction, and various parameters were optimized. We first investigated the oxidation of benzyl alcohol to benzaldehyde using a  $RuCl_3 \cdot 3H_2O/base$  catalyst system, and the results are summarized in Table 1.

As shown in Table 1, amines can play an important role in the RuCl<sub>3</sub>-catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde and have a dramatic influence on the benzaldehyde yield. For example, when amines were not employed as the base in the reactions, the benzaldehyde product was afforded in less than 5% yield (Table 1, entry 1). Furthermore, the desired product was not detected when  $K_2CO_3$  was used as the base (Table 1, entry 6). To our delight, the oxidation reaction was greatly enhanced by certain amines, with dicyclohexylamine (DCHA) being the most effective amine base. When 5 mol% RuCl<sub>3</sub> · 3H<sub>2</sub>O was used in tetrahydrofuran (THF) at rt for 48 h with DCHA as a base (Table 1, entry 5), an excellent yield of

Table 1. RuCl<sub>3</sub>-catalyzed aerobic oxidation of benzyl alcohol<sup>a</sup>

ОН	RuCl <sub>3</sub> •3H <sub>2</sub> O	СНО
	Base, THF, rt, air	

Entry	Base	$RuCl_3 \cdot 3H_2O \ (mol\%)$	Isolated yield (%) <sup>b</sup>
1	_	5	<5
2	Et <sub>3</sub> N	5	19 (26)
3	Diethylamine	5	30 (32)
4	TMEDA	5	59 (60)
5	DCHA	5	85 (82)
6	K <sub>2</sub> CO <sub>3</sub>	5	0
7	DCHA	2	33 (31)
8	DCHA	3	37 (38)
9	DCHA	6	86 (82)

<sup>a</sup>The reaction was performed with benzyl alcohol (1 mmol) and base (1.0 mmol) in 1 mL of THF at rt for 48 h.

<sup>b</sup>The values in parentheses are the yields determined by <sup>1</sup>H NMR using nitromethane as internal standard.

85% was afforded. To further examine the effects of the amines on the reaction, a variety of amines were chosen as the base. Many other amines, including trimethylamine, diisopropylamine, aniline, *N*,*N*-dimethyl aniline, *N*,*N*-diethyl ethylenediamine, imidazole, triethanolamine, 3-amino-1,2,4-trizole, *tri-n*-propylamine, *tri-n*butylamine, pyridine, and pyridine hydrochloride, were also screened, but the results were unsatisfactory. The influence of the loading of RuCl<sub>3</sub> · 3H<sub>2</sub>O was also evaluated. Good results were obtained when 5 mol% RuCl<sub>3</sub> · 3H<sub>2</sub>O catalyst was used. Interestingly, when more than 5 mol% of the RuCl<sub>3</sub> · 3H<sub>2</sub>O (Table 1, entry 9) catalyst was employed, there was no visible effect on the reaction yield. However, when the catalytic loading was decreased to 2 mol%, the yield was significantly decreased to 33% (Table 1, entry 7).

Efforts were next directed toward investigating the solvent effects. After examining different solvents including THF, ethylene glycol dimethyl ether (GDE),  $CH_2Cl_2$ ,  $C_6H_6$ , and  $CHCl_3$ , THF was found to be the optimal solvent (Table 2, entry 1). The reaction provided an excellent yield of 88% when THF was used. Subsequently, the influence of the amount of DCHA was evaluated. As shown in Table 2, the amount of DCHA had a significant impact on the yield. Good results were obtained when 1.0 equiv of DCHA was used. However, when the amount of DCHA was decreased to 0.2 equiv, the yield significantly decreased to 55% (Table 2, entry 8), indicating that any further decrease in the amount of DCHA will most likely lead to lower yields. To improve the reaction rate, the oxidation of benzylalcohol was treated at 40 °C, and the yield significantly decreased (Table 2, entries 9 and 10).

**Table 2.** Optimization of the reaction conditions $^{a}$ 

CHO

OH RuCl<sub>3</sub>•3H<sub>2</sub>O

	DCHA, II, all		
Entry Solvent DCHA	Isolated yield (%) <sup>b</sup>		
1 THF 1.0 equiv	88 (85)		
2 $GDE^c$ 1.0 equiv	83 (79)		
3 $CH_2Cl_2$ 1.0 equiv	82 (83)		
4 $C_6H_6$ 1.0 equiv	75 (67)		
5 CHCl <sub>3</sub> 1.0 equiv	50 (55)		
6 THF 1.2 equiv	86 (84)		
7 THF 0.8 equiv	83 (76)		
8 THF 0.2 equiv	55 (53)		
9 THF 1.0 equiv	$54(52)^d$		
10 THF 1.0 equiv	$52(53)^e$		

10	IHF	1.0 equiv	52 (53)
"The reaction	n was parformed with her	and RuCl 2H (	(0.05  mmal) in $1  mI$

"The reaction was performed with benzyl alcohol (1 mmol) and  $RuCl_3 \cdot 3H_2O$  (0.05 mmol) in 1 mL of solvent at rt for 4 days.

<sup>b</sup>The values in parentheses are the yields determined by <sup>1</sup>H NMR using nitromethane as internal standard.

<sup>c</sup>Ethylene glycol dimethyl ether.

 $^{d}$ The reaction was performed with benzylalcohol (1 mmol) and RuCl<sub>3</sub>·3H<sub>2</sub>O (0.05 mmol) in 1 mL of solvent at 40 °C for 2 days.

 $^{c}$ The reaction was performed with benzylalcohol (1 mmol) and RuCl<sub>3</sub> · 3H<sub>2</sub>O (0.05 mmol) in 1 mL of solvent at 40  $^{\circ}$ C for 4 days.

Based on these observations, the optimum reaction conditions for the oxidation were found to be 0.05 equiv of  $RuCl_3 \cdot 3H_2O$ , 1.0 equiv of DCHA, with THF as the solvent at rt.

Using the optimal reaction conditions, the scope of the reaction was next examined, and the results are summarized in Table 3. As shown in Table 3, many benzylic alcohols were oxidized to their corresponding aldehydes in moderate to excellent yields under the optimized conditions. It is worthy of note that this catalyst system showed compatibility with various groups such as Cl, Br, CH<sub>3</sub>, CH<sub>3</sub>O, CF<sub>3</sub>, CN, NO<sub>2</sub>, and NHCOCH<sub>3</sub>. The system is especially favorable with an OH group substituted on the benzene ring. The results have shown that electronegativities of the substituents played a major role in governing the reactivity of the substrates. With electron-donating substituents on the benzylic alcohols, increased yields of products were observed (Table 3, entries 3–7). For example, *p*-methoxylbenzyl alcohol was oxidized to *p*-methoxyl benzaldehyde with a yield of 90% (Table 3, entry 6). Electron-withdrawing groups (e.g., NO<sub>2</sub>, CN, CF<sub>3</sub>) on the benzylic alcohols

Table 3. RuCl<sub>3</sub>-catalyzed aerobic oxidation of benzylic alcohols<sup>a</sup>



Entry	Compound	$R^1$	$\mathbb{R}^2$	Time (days)	Yield (%) <sup>b</sup>
1	2a	Н	Н	2	$82^c$
2	2b	o-CH <sub>3</sub>	Н	4	72
3	2c	m-CH <sub>3</sub>	Н	4	86
4	2d	p-CH <sub>3</sub>	Н	4	88
5	2e	m-OCH <sub>3</sub>	Н	4	89
6	2f	p-OCH <sub>3</sub>	Н	4	90
7	2g	<i>p</i> -OH	Н	4	85
8	2h	m-Cl	Н	4	70
9	2i	p-Cl	Н	4	82
10	2j	o-Br	Н	4	80
11	2k	$o-NO_2$	Н	4	40
12	21	$m-NO_2$	Н	4	44
13	2m	$p-NO_2$	Н	4	36
14	2n	<i>m</i> -CN	Н	4	45
15	20	p-CN	Н	4	43
16	2p	p-CF <sub>3</sub>	Н	4	41
17	2q	m-NHCOCH <sub>3</sub>	Н	4	70
18	2r	p-NHCOCH <sub>3</sub>	Н	4	75
19	2s	H	$CH_3$	4	30
20	2t	Н	Ph	4	26

<sup>*a*</sup>The reaction was performed with benzyl alcohol (1 mmol) and  $RuCl_3 \cdot 3H_2O$  (0.05 mmol) in 1 mL of THF at rt.

<sup>b</sup>Isolated yield.

<sup>c</sup>Yield was determined by <sup>1</sup>H NMR using nitromethane as internal standard.



Scheme 1. Oxidation of cinnamic alcohol and furfuryl alcohol.

inhibited the oxidation, affording the corresponding aldehydes in poor yields (Table 3, entries 11-16). For instance, the yield of *p*-nitrobenzaldehyde decreased to 36% when *p*-nitrobenzyl alcohol was oxidized under the same reaction conditions.

Although the oxidation took place at a slow pace, it was conducted under mild conditions. It is noteworthy that the  $RuCl_3 \cdot 3H_2O/DCHA$  system displayed a preference for the primary versus secondary benzylic alcohols. As observed in the oxidation of the secondary benzylic alcohols, 2-phenylethanol (Table 3, entry 19), and benzohydrol (Table 3, entry 20), poor yields were obtained under the same reaction conditions. Our results suggested that steric nature of the substrates played an important role in the oxidation process.

In addition, as shown in Scheme 1, cinnamic alcohol was resistant to oxidation and the  $RuCl_3 \cdot 3H_2O/DCHA$  system is a poor catalyst for the aerobic oxidation of furfuryl alcohol to furfural under standard reaction conditions. These results showed again that the  $RuCl_3 \cdot 3H_2O/DCHA$  system has selectivity for benzylic alcohols.

To obtain more information about the selectivity of  $RuCl_3 \cdot 3H_2O/DCHA$  system in oxidation of primary benzylic alcohols and secondary benzylic alcohols, the intermolecular and intramolecular competition experiments between primary and secondary benzylic alcohols were designed. As seen from Scheme 2,  $RuCl_3 \cdot 3H_2O/DCHA$  system oxidized primary benzylic alcohols with high selectivity. In addition to the intermolecular competition experiment, the same behavior was observed in the intramolecular competition of two primary/secondary diols, 4-(1'-hydroxyethyl)-benzyl alcohol **3** and 3-(1'-hydroxyethyl)benzyl alcohol **6**. As shown in Scheme 3, the  $RuCl_3 \cdot 3H_2O/DCHA$  system again displayed a preference for the primary versus the



Scheme 2. Intermolecular competition oxidation.



Scheme 3. Intramolecular competition oxidation.

secondary hydroxyl group of a benzylic diol. Notably, we observed that the selectivity for the primary hydroxyl group of **6** was greater than **3**.

In conclusion, we have developed a mild procedure for the direct aerobic oxidation of benzylic alcohols using  $RuCl_3 \cdot 3H_2O/DCHA$ , a simple combination of commercially available reagents. Under ambient atmosphere and at room temperature, primary benzylic alcohols were transformed to the corresponding aldehydes in moderate to excellent yields. It is noteworthy that the  $RuCl_3 \cdot 3H_2O$ –DCHA system displayed a preference for the primary versus secondary benzylic alcohols in both intermolecular and intramolecular competition experiments. The present protocol is mild and selective as compared to previously reported literature methods. Further investigations are under way to formulate a plausible reaction mechanism.

#### **EXPERIMENTAL**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker 400 spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in  $\delta$  (ppm) units downfield from TMS. RuCl<sub>3</sub> · 3H<sub>2</sub>O, DCHA, alcohols and other reagents were all purchased from commercial sources.

# Typical Experimental Procedure for Oxidation of Benzylic Alcolols Using RuCl<sub>3</sub> · 3H<sub>2</sub>O/DCHA

DCHA (1.0 mmol) was added dropwise to a solution of benzylic alcohol (1.0 mmol) and  $RuCl_3 \cdot 3H_2O$  (0.05 mmol) in THF (1 mL) under an air atmosphere, and the mixture was stirred at room temperature (monitored by thin-layer chromatography, TLC). Then, the solvent was removed under reduced pressure, and the crude product was purified by silica-gel column chromatography to provide the desired product.

#### **Characterization Data of Typical Products**

**3-Cyanobenzaldehyde (2n).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.70 (t, J = 7.7 Hz, 1H, Ar-H), 7.92 (dt, J = 7.7, 1.2 Hz, 1H, Ar-H), 8.13 (dt,

J = 7.7, 1.2 Hz, 1H, Ar-H), 8.17 (t, J = 1.2 Hz, 1H, Ar-H), 10.05 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  113.7, 117.6, 130.1, 133.1, 133.3, 136.9, 137.2, 190.0 (CO).

**4-Cyanobenzaldehyde (20).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.84 (dd, J = 6.8, 1.6 Hz, 2H, Ar-H), 7.99 (dd, J = 6.8, 1.6 Hz, 2H, Ar-H), 10.09 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  117.6, 117.7, 129.9, 132.9, 138.7, 190.7 (CO).

**4-(Trifluoromethyl)benzaldehyde (2p).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (d, J = 8.0 Hz, 2H, Ar-H), 8.00 (d, J = 8.0 Hz, 2H, Ar-H), 10.09 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  123.4 (q, J = 272.9 Hz, CF<sub>3</sub>), 126.0 (q, J = 3.7 Hz), 129.9, 135.5 (q, J = 32.5 Hz), 138.6, 191.1 (CO).

**3-Acetamidobenzaldehyde (2q).** White waxy solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.21 (s, 3H, CH<sub>3</sub>), 7.45 (t, J = 7.9 Hz, 1H, Ar-H), 7.59 (d, J = 7.9 Hz, 1H, Ar-H), 7.88 (d, J = 7.9 Hz, 1H, Ar-H), 8.04 (s, 1H, Ar-H), 8.45–8.55 (br s, 1H, NH), 9.94 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  24.4, 120.4, 125.7, 125.9, 129.7, 136.9, 139.1, 169.4, 192.4.

**4-Acetamidobenzaldehyde (2r).** White waxy solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.24 (s, 3H, CH<sub>3</sub>), 7.72 (d, J = 8.5 Hz, 2H, Ar-H), 7.76–7.83 (br s, 1H, NH), 7.86 (d, J = 8.5 Hz, 2H, Ar-H), 9.93 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  24.8, 119.2 (2C), 131.2 (2C), 132.2, 143.6, 168.7, 191.1.

**4-(1'-Hydroxyethyl)benzaldehyde (4).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.49 (d, J = 6.5 Hz, 3H, CH<sub>3</sub>), 2.53–2.56 (br s, 1H, OH), 4.96 (q, J = 6.5 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H, Ar-H), 7.82 (d, J = 8.2 Hz, 2H, Ar-H), 9.94 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  25.3, 69.8, 125.9 (2C), 130.1 (2C), 135.5, 152.9, 192.2 (CO).

**4-Acetylbenzaldehyde (5).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.68 (s, 3H, CH<sub>3</sub>), 8.00 (d, J = 8.0 Hz, 2H, Ar-H), 8.12 (d, J = 8.0 Hz, 2H, Ar-H), 10.1 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  27.0, 128.8 (2C), 129.8 (2C), 139.1, 141.2, 191.6 (CHO), 197.4 (CO).

**3-(1'-Hydroxyethyl)benzaldehyde (7).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.51 (d, J = 6.5 Hz, 3H, CH<sub>3</sub>), 2.55 (s, 1H, OH), 4.97 (q, J = 6.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H, Ar-H), 7.65 (dt, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.76 (dt, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.87 (t, J = 1.2 Hz, 1H, Ar-H), 9.98 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  25.4, 69.7, 126.5, 128.9, 129.2, 131.7, 136.5, 147.0, 193.5 (CO).

**3-Acetylbenzaldehyde (8).** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.69 (s, 3H, CH<sub>3</sub>), 7.68 (t, J = 7.7 Hz, 1H, Ar-H), 8.11 (dt, J = 7.7, 1.4 Hz, 1H, Ar-H), 8.25 (dt, J = 7.7, 1.4 Hz, 1H, Ar-H), 7.87 (t, J = 1.4 Hz, 1H, Ar-H), 10.1 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  26.7, 129.5, 129.6, 133.7, 133.8, 136.6, 137.8, 191.5, 197.0.

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