

Selective Aerobic Oxidation of Primary Alcohols Catalyzed by a $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ /Hydroquinone System

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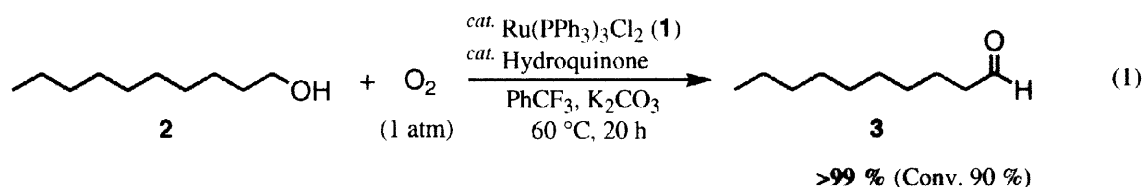
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Abstract: Aerobic oxidation of primary alcohols to aldehydes was efficiently performed using a $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ /hydroquinone system under atmospheric oxygen at 60 °C. A primary alcohol even in the presence of a secondary one was selectively oxidized to the corresponding aldehyde in high yield.

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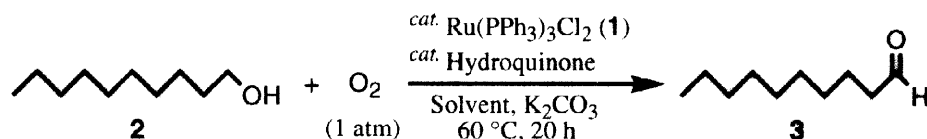
Aerobic oxidation of organic compounds utilizing molecular oxygen as the oxidant will become more important in synthetic organic chemistry from both economical and environmental points of view. Selective oxidation of alcohols to aldehydes is an important fundamental transformation in organic synthesis. There have been several works on the stoichiometric and catalytic oxidation of alcohols to carbonyl compounds by ruthenium complexes.¹⁾ However, very little investigation on aerobic oxidation of saturated primary alcohols other than activated alcohols such as allylic or benzylic alcohols has been carried out.²⁾ More recently, aerobic oxidation of primary alcohols catalyzed by ruthenium complexes^{2c,d)} and copper catalysts³⁾ has been reported.

We now find that a $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ /hydroquinone system is an efficient catalytic system for the selective oxidation of primary alcohols to aldehydes under atmospheric oxygen (eq. 1).



A typical reaction was carried out as follows : Alcohol (2 mmol) was added to a solution of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (1) (0.2 mmol), hydroquinone (0.2 mmol), and K_2CO_3 (0.06 mmol) in trifluorotoluene (6 mL), and the mixture was stirred under oxygen atmosphere (1 atm) at 60 °C for 20 h. Products were isolated by column chromatography on silica gel with hexane/ethyl acetate (10/1).

Table 1 shows the representative results for the aerobic oxidation of 1-decanol (2) in the presence of a catalytic amount of various ruthenium complexes under several conditions. The oxidation of 2 using 1 combined with hydroquinone as a catalyst in trifluorotoluene under 1 atm of oxygen at 60 °C for 20 h afforded decanal (3) in >99% selectivity at 90% conversion (Run 1). Among the solvents examined, PhCF_3

**Table 1.** Oxidation of 1-Decanol(**2**) to Decanal(**3**) under Various Reaction Conditions^{a)}

Run	Catalyst	Solvent	Conv. / %	Select. / %
1	Ru(PPh ₃) ₃ Cl ₂ (1)	PhCF ₃	90	>99
2	1	toluene	85	98
3	1	(CH ₂ Cl) ₂	70	93
4	1	AcOEt	60	98
5	1	dioxane	47	77
6	1	THF	44	77
7	1	CH ₃ CN	8	100
8 ^{b)}	1	PhCF ₃	51	98
9 ^{c)}	1	PhCF ₃	70	97
10	RuCl ₃ ·nH ₂ O	PhCF ₃	24	0
11	[Ru(<i>p</i> -cymene)Cl ₂] ₂	PhCF ₃	0	0
12	Ru(DMSO) ₄ Cl ₂	PhCF ₃	7	>99
13	Pr ₄ N ⁺ RuO ₄ ⁻ (TPAP)	PhCF ₃	98	41

^{a)} **2** (1 mmol) was allowed to react with O₂ (1 atm) in the presence of catalyst (0.2 mmol) and hydroquinone (0.2 mmol), K₂CO₃ (0.03 mmol) in solvent (6 mL) at 60 °C for 20 h. ^{b)} In the absence of hydroquinone. ^{c)} In the absence of K₂CO₃.

was found to be the best solvent, followed by benzene, (CH₂Cl)₂ and AcOEt. However, the reaction in polar solvents such as dioxane, THF and CH₃CN led to unfavorable results (Runs 5-7). In the absence of either hydroquinone or K₂CO₃, **2** gave **3** in moderate conversions (Runs 8 and 9). The oxidation of **2** by several ruthenium complexes such as RuCl₃·nH₂O, Ru(DMSO)₄Cl₂, [Ru(*p*-cymene)Cl₂]₂, and tetrapropylammonium perruthenate (Pr₄N⁺RuO₄⁻) was examined, but these complexes were found to be less efficient than **1** (Runs 10-13).

The oxidation of secondary alcohols to the corresponding ketones by ruthenium catalysts has been reported by Bäckvall.^{2a,b)} However, in the present ruthenium/hydroquinone-catalyzed oxidation, primary

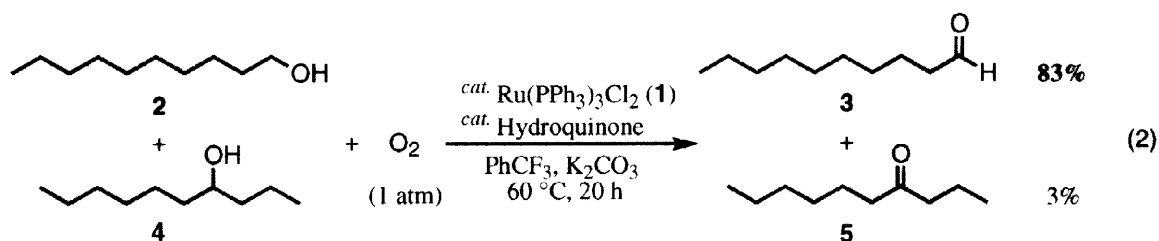

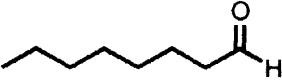
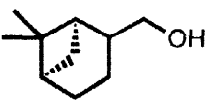
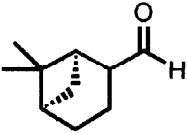
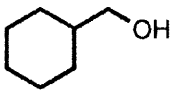
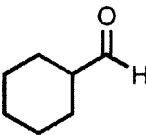
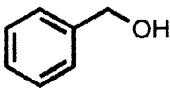
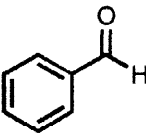
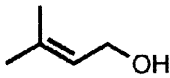
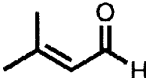
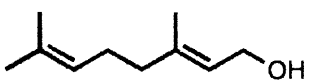
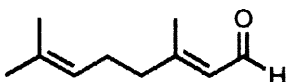
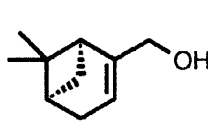
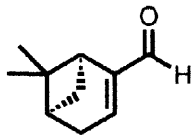
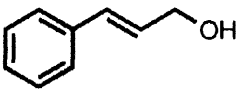
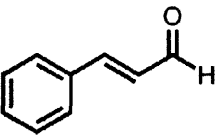


Table 2. Aerobic Oxidation of Alcohols by the Catalyzed $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ / Hydroquinone System^{a)}

Run	Substrate	Product	Conv. / %	Select. / %
1 ^{b)}			90	>99
2 ^{b)}			80	95
3 ^{b)}			72	>99
4			80	>99
5			94	86
6			>99	99
7			92	98
8			100	>99

^{a)} Alcohol (2 mmol) was allowed to react with O_2 (1 atm) in the presence of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (**1**) (0.2 mmol) and hydroquinone (0.2 mmol), K_2CO_3 (0.06 mmol) in trifluorotoluene (6 mL) at 50 °C for 15 h. ^{b)} Reaction was carried out using **1** (0.4 mmol) and hydroquinone (0.4 mmol) at 60 °C for 20 h.

alcohols were selectively oxidized even in the presence of secondary ones, *e.g.*, treatment of a mixture of **2** and 4-decanol (**4**) by the present catalytic system produced **3** (83%) in preference to 4-decanone (**5**) (3%) (eq. 2).

Table 2 shows the results for the oxidation of various primary alcohols with dioxygen in the presence of catalytic amounts of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ and hydroquinone at 50 or 60 °C. Aliphatic and cyclic primary alcohols were oxidized to aldehydes in good yields, *e.g.*, oxidation of (-)-myrtanol gave (-)-myrtanal in 95% selectivity at 80% conversion. Allylic alcohols were converted into the corresponding unsaturated aldehydes in high yields without intramolecular hydrogen transfer (Runs 5-8), although some ruthenium(II) phosphine complexes are known to catalyze intramolecular hydrogen transfer reactions

of allylic alcohols to saturated ketones.⁴⁾

The formation of an alkoxy-ruthenium complex is known to be important for the selective oxidation of primary alcohols to aldehydes.⁵⁾ In the present ruthenium/hydroquinone system, the oxidation is assumed to proceed via the formation of a similar alkoxy-ruthenium complex, since primary alcohols were preferentially oxidized in the presence of secondary ones.

Bäckvall *et al.*^{1g)} have reported that in the aerobic oxidation of benzyl alcohol by a triple catalytic system consisting of RuCl(OAc)(PPh₃)₃/hydroquinone/Co(salophen)(PPh₃), the Ru complex dehydrogenates benzyl alcohol to benzaldehyde, and the resulting "RuH₂" reacts with benzoquinone to form the "Ru" complex and hydroquinone which then is reoxidized to benzoquinone with O₂ under the influence of Co(salophen)(PPh₃). Although it seems rather difficult to propose the actual active species involved in this reaction, Ru(PPh₃)₃Cl₂ is thought to react with benzoquinone, giving a new Ru species which can smoothly oxidize primary alcohols to aldehydes. The formation of the new Ru species is supported by the rapid color change of the catalyst solution involving Ru(PPh₃)₃Cl₂ from brown to green when benzoquinone was added. Much work on the reaction pathway still remains.

In summary, we have found that an aerobic oxidation of primary alcohols to aldehydes is achieved using Ru(PPh₃)₃Cl₂/hydroquinone as the catalyst even in the presence of secondary alcohols.

Acknowledgment

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