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A Novel Environmentally Benign Method for the Selective Oxidation of Alcohols to Aldehydes and Ketones

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Abstract: In the presence of [Ru(terpyridine)(2,6-pyridinedicarboxylate)], aliphatic and benzylic alcohols are oxidized to the corresponding aldehydes or ketones with high selectivity by using hydrogen peroxide as the oxidant. There is no need for the addition of co-catalysts or organic solvents. By applying an optimized reaction protocol, high catalyst productivity (turnover number > 10000) and activity (turnover frequency up to 14800 h^{-1}) has been achieved.

Keywords: alcohols · aldehydes · homogeneous catalysis · oxidation · ruthenium

Introduction

Aldehydes and ketones are important precursors and intermediates for the pharmaceutical and fine-chemical industries. They are particularly useful for the production of flavors, fragrances, and biologically active compounds.[1] Traditionally, these carbonyl derivatives are produced through the selective oxidation of alcohols with a stoichiometric amount of chromium salts[2] or other oxidants such as oxalyl chloride[3] and hypervalent iodines.[4] The application of these procedures, however, caused severe environmental problems due to waste from heavy metals or stoichiometric amounts of reagents and the generation of undesirable co-products. From the standpoint of green and sustainable chemistry, there is still a need to develop cleaner catalytic oxidation systems for this reaction. Obviously, the choice of the "green" oxidant determines the environmental impact of an oxidation process to a significant extent. In general, molecular oxygen is the ideal oxidant, and many processes were developed with oxygen or air as oxidant in the presence of Ru,[5] Pd,[6] Co,[7] Cu,[8] Pt,[9] Rh,[10] V,[11] Os,[12] Ce,[13] Ni,[14] Mo,[15] or $Br_2/NaNO_2$.[16] However, the use of O_2 is sometimes difficult to control and may result in combustion. Furthermore, in most cases only one of the two oxygen atoms in O_2 is used productively for oxidation. Thus, an (over)stoichiometric amount of co-reductant is needed for these processes.

Besides molecular oxygen, hydrogen peroxide (H_2O_2) is a "green", waste-avoiding oxidant.[17] It can oxidize organic compounds with an atom efficiency of 47% and theoretically generates only water as co-product. Notably, H_2O_2 is much easier to handle, especially for batch reactions. Hence, H_2O_2 is particularly useful for liquid-phase oxidations for the synthesis of fine chemicals and electronic materials as well as pharmaceuticals and agrochemicals. However, there is also a clear recent trend to use H_2O_2 for bulk processes, for example, the production of propylene oxide.[18]

Comparably few processes with H_2O_2 as the oxidant for the selective oxidation of alcohols have been described to date.[19] A drawback of all the procedures known are the large amounts of organic solvents needed for selective reactions. Thus, the development of practical, clean, and highly efficient catalysts for such processes is highly desirable and challenging.

Results and Discussion

Recently, we developed novel catalysts for epoxidations with hydrogen peroxide.[20] Based on these results, we report herein the first ruthenium-catalyzed oxidation of alcohols to aldehydes and ketones with hydrogen peroxide as the oxidant without the addition of co-catalyst or organic solvent (Scheme 1).

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$$R_1CH(OH)R_2 + 30\ wt\%\ H_2O_2 \xrightarrow{[Ru]} R_1COR_2$$

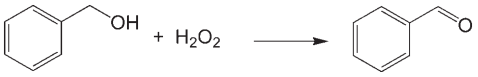
Scheme 1. Ruthenium-catalyzed oxidation of alcohols.

Our previous results showed that ruthenium(II) complexes with tridentate nitrogen ligands such as terpyridine (terpy), pyridine-2,6-bisoxazoline (pybox), and pyridine-2,6-bisimidazoline (pybim) are efficient catalysts for olefin oxidation.[20,21] Hence, we became interested in utilizing these complexes in the selective oxidation of alcohols.

In exploratory experiments, the reaction of benzyl alcohol with hydrogen peroxide in the presence of ruthenium complexes **1**–**4** (Scheme 2)[20c,21] was examined. To our delight, the model reaction proceeded smoothly in the presence of 0.01 mol% catalyst at room temperature in 1 h without any additional solvent or co-catalyst. Among the various Ru complexes used, [Ru^{II}(terpy)(2,6-pyridinedicarboxylate)] (**1**) showed the best activity. Thus, we further optimized the reaction conditions in the presence of **1**, that is, the amount of catalyst, reaction temperature, and the ratio of hydrogen peroxide to benzyl alcohol. It was observed that the reaction temperature (0–40 °C) had only an insignificant effect on the yield of benzaldehyde (Table 1, entries 1–4). With respect to the catalyst concentration, even with only 0.0025 mol% of **1**, benzaldehyde was obtained in 37% yield with 100% chemoselectivity (Table 1, entry 5).

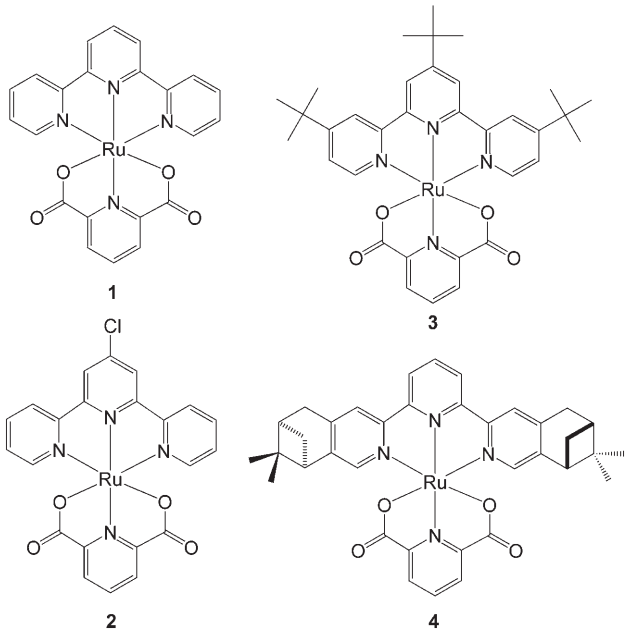
Interestingly, with higher catalyst loading (0.1 mol%), the yield of benzaldehyde dropped to 68% yield (Table 1, entry 9). This effect is attributed to faster decomposition of the hydrogen peroxide through a second-order pathway with respect to Ru.[20h] Increasing the amount of hydrogen peroxide improved the reaction effectively. The most-suitable ratio of hydrogen peroxide to benzyl alcohol was found to be 1:2.5. Under these conditions, the yield of benzaldehyde reached 92% with 8% benzoic acid as by-product (Table 1, entries 12–13). A longer reaction time (2 h) or continuous addition of hydrogen peroxide did not improve the product yield (Table 1, entries 14–15). Complexes **2**–**4** were also tested under the optimized conditions to compare the effect of the ligand. All the Ru complexes prepared catalyzed the oxidation of benzyl alcohol to give the corresponding benzaldehyde in very good yields (Table 1, entries 16–18). However, the addition of aliphatic substituents to the terpyridine rings, which increases the solubility of the complex, caused a lower product yield due to further oxidation of the aldehyde to benzoic acid. Notably, the turnover number (ton) of the ruthenium catalyst reached 14800 when 0.0025 mol% of **1** was employed. Compared with the productivities of the Ru catalysts usually reported (ton = 10–500),[5] this is to the best of our knowledge one of the highest values reported for the selective oxidation of benzyl alcohol to benzaldehyde.

Table 1. Selective oxidation of benzyl alcohol to benzylaldehyde.



Entry	Catalyst ([mol%])	Alcohol/H_2O_2 [mol/mol]	T [°C]	t [h]	Conv.[a] [%]	Yield[b] [%]	ton[c]
1	–	1:1	RT	1	trace	–	–
2	**1** (0.01)	1:1	0	1	63	63	6300
3	**1** (0.01)	1:1	RT	1	75	74	7400
4	**1** (0.01)	1:1	40	1	68	68	6800
5	1 (0.0025)	1:1	RT	1	37	37	14800
6	**1** (0.005)	1:1	RT	1	61	61	12000
7	**1** (0.04)	1:1	RT	1	74	74	1850
8	**1** (0.07)	1:1	RT	1	75	73	1000
9	**1** (0.1)	1:1	RT	1	68	68	680
10	**1** (0.01)	1:1.2	RT	1	80	80	8000
11	**1** (0.01)	1:1.5	RT	1	85	82	8500
12	**1** (0.01)	1:2	RT	1	93	88	9300
13	**1** (0.01)	1:2.5	RT	1	99	92	9900
14	**1** (0.01)	1:1	RT	2	76	75	7600
15[d]	**1** (0.01)	1:1	RT	1	70	70	7000
16	**2** (0.01)	1:2.5	RT	1	83	78	8300
17	**3** (0.01)	1:2.5	RT	1	98	75	9800
18	**4** (0.01)	1:2.5	RT	1	100	68	10000

[a] Conversion of benzyl alcohol. [b] Yield of benzylaldehyde based on benzyl alcohol determined by GC. [c] Turnover number = number of moles of alcohol converted per mole of ruthenium. [d] H_2O_2 was added continuously over 1 h.



Scheme 2. Ruthenium catalysts tested for alcohol oxidation.

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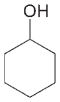
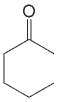
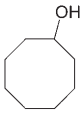
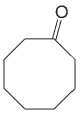
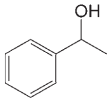
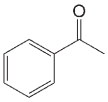
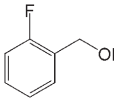
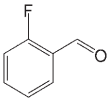
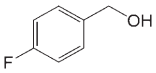
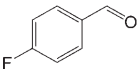
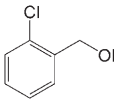
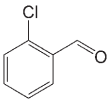
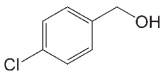
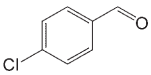
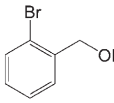
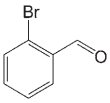
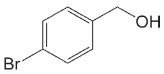
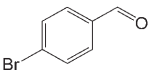
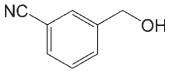
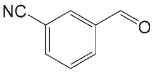
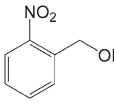
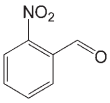
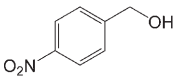
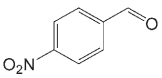
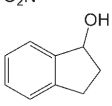
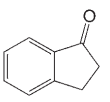
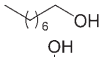
To demonstrate the usefulness of our novel protocol, the easily available and effective catalyst **1** was further employed in the selective oxidation of different alcohols (Table 2).[22] Cycloalcohols and various substituted benzyl alcohols were chosen as representative substrates.

Firstly, the selective oxidation of several aliphatic alcohols such as cyclopentanol, cyclohexanol, and cyclooctanol was performed. All these alcohols gave excellent results, and the corresponding ketones were obtained in 90–93% yield (Table 2, entries 1–3). Importantly, the reactions with cyclopentanol and cyclohexanol as starting materials should be well-sealed to prevent evaporation of the starting materials. As expected, the reaction rate was lower when secondary alcohols were oxidized, possibly due to steric reasons. Nevertheless, by applying longer reaction times (24–48 h), 1-phenylethanol was oxidized to acetophenone in good yield (89%) (Table 2, entry 4).

As shown by the oxidation of substituted benzyl alcohols, the reaction tolerates a considerable number of functional groups and substitution patterns. All halogen-substituted benzyl alcohols (fluorine, chlorine, and bromine) gave very good results (75–93% yield) at the *ortho* and *para* positions (Table 2, entries 5–10). However, the catalytic activity changed severely when the substituents were changed. More specifically, the catalytic activity decreased in the sequence F > Cl > Br. Hence, for the fluoride-substituted benzyl alcohol, the reaction time was 0.4–1 h, but for the bromide-substituted benzyl alcohols, 16–28 h were needed for the reaction. Moreover, higher reactivity was exhibited for *ortho*-halogen-substituted benzyl alcohols. Whereas the *ortho*-bromobenzyl alcohol oxidized in 16 h at room temperature, the *para*-substituted one needed 28 h for 95% conversion even at 60 °C. Oxidation of highly electron deficient CN- or NO_2-substituted benzyl alcohols was also performed (85–94% yield) (Table 2, entries 11–14). For the oxidation of 1-indanol to 1-indanone, 94% conversion and 75% yield was achieved. However, this catalyst system showed no activity for the selective oxidation of primary or secondary noncyclic aliphatic alcohols (Table 2, entries 15 and 16).

Table 2. Selective oxidation of alcohols to aldehydes or ketones with **1**.

Entry	Substrate	Product	*T* [°C]	*t* [h]	Conv.[a] [%]	Yield[b] [%]
1			RT	24	99	98
2			40	24	93	91
3			60	19	93	93
4			RT	48	96	89
5			RT	0.4	95	90
6			RT	1	96	92
7			RT	16	98	93
8			40	18	94	75
9			RT	16	98	93
10			60	28	95	81
11			RT	1	94	94 (94)[c]
12			RT	24	91	80
13			60	4	95	81
14			40	48	94	75
15			60	72	0	0
16			60	72	0	0

[a] Conversion of alcohol. [b] Yield of aldehyde based on alcohol determined by GC. [c] Yield of isolated product.

Conclusions

In summary, we have developed easy-to-use ruthenium catalysts for the selective oxidation of alcohols to the corresponding aldehydes and ketones. The method presented should be especially useful for environmentally benign oxidation to give substituted benzaldehydes, which are important fine-chemical intermediates. Compared to previous protocols, this catalyst system has the advantage that no organic solvents or co-catalysts are necessary. This makes the reaction more practical and easily manageable. The scope of the catalyst has been demonstrated in the selective oxidation of 15 different substrates. High yield and chemoselectivity (often $\approx 90\,\%$) were achieved in most cases. Notably, the catalyst turnover numbers were all around 10000; this makes it one of the most-effective catalysts for the selective oxidation of alcohols known thus far.

Acknowledgements

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[22] Experimental procedure: All reactions were carried out in oil (25–60 °C). Benzyl alcohol (0.541 g, 5 mmol), **1** (0.25 mg, 0.0005 mmol), and H_2O_2 ($\approx$1.28 mL, 12.5 mmol, 30 wt %) were added to a glass reactor (40 mL). The reactor was carefully sealed to avoid evaporation of chemicals during reaction. The reaction mixture was vigorously stirred (750 rpm) at 25 °C for 1 h. After the reaction, a two-layer mixture was obtained (organic phase/water phase), and dodecane ($\approx$0.85 g, 5 mmol) and acetone (50 mL) were added to dissolve the mixture for analysis. Quantitative GC analysis was conducted with a GC-FID chromatograph (HP6890N with FID detector, column HP5 30 m $\times$ 0.250 mm $\times$ 0.25 μm) and an external-standard method. The identity of the product was further confirmed by GC–MS (HP6890N with MSD5973, column HP5MS 30 m $\times$ 0.250 mm $\times$ 0.25 μm) and compared with an authentic sample of benzaldehyde. All the other reactions were analyzed with the same method. For GC comparison, commercial samples of the products were used. The products were easily isolated by diethyl ether extraction followed by column chromatography. For example, 3-formylbenzonitrile was isolated in 94 % yield. 3-Formylbenzonitrile: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.70 (t, J = 7.74 Hz, 1H), 7.78–7.95 (m, 1H), 8.11–8.16 (m, 1H), 8.16–8.20 (m, 1H), 10.04 ppm (s, 1H).

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