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An efficient oxidation method for conversion of alcohols to their corresponding carboxylic acids and ketones using oxone as co-oxidant

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Abstract

An efficient and practical method for the conversion of alcohols to their corresponding carboxylic acids and ketones via a ruthenium chloride-catalyzed oxidation process has been developed. The reaction proceeded under mild reaction condition using environmentally friendly oxone as a co-oxidant. Various alcohols were examined to provide the desired products in good yields.

Key words: Alcohol; carboxylic acid; ketone; oxidation; oxone.

Introduction

The oxidation of primary and secondary alcohols to their corresponding carboxylic acids and ketones respectively, is one of the most fundamental reactions in organic synthesis.[1] Various reagents have been developed and used as an oxidant for this transformation which include Jones,[2a-c] PDC in DMF,[2d] $RuCl_3/H_5IO_6$,[3] CrO_3/H_5IO_6,[4] RuO_4,[5] $RuCl_3/K_2S_2O_8$,[6] Ru-Co bimetallic catalyzed oxidation,[7] $Cu(MnO_4)_2$ oxidation,[8] TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy)-catalyzed oxidation with sodium hypochlorite[9a-c] and bis(acetoxy)iodobenzene (BAIB),[9d,e] Na_2WO_4/H_2O_2,[10] Cu(II)-salen complex/H_2O_2,[11] CuCl/^{t}BuOOH (in decane),[12] PCC/H_5IO_6,[13a] and $VO(acac)_2$/Cu(II) 2-ethylhexanoate/DABCO/O_2 in [bmim]OTf.[13b] But, all of these have some limitation such as strongly basic or acidic condition, used of costly and/or toxic oxidizing agent, production of undesirable side reaction, elevated temperatures and long reaction time. Therefore, alternative methods are still desirable from economic and environmental point of view.

Oxone consists of $2KHSO_5.KHSO_4.K_2SO_4$; its active component is potassium peroxymonosulfate ($KHSO_5$). It is an effective oxidant which has proved to be a versatile reagent for various

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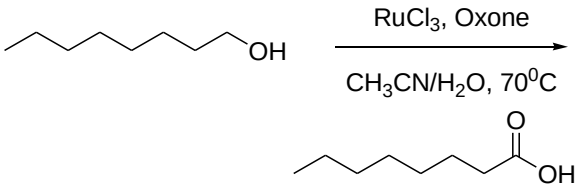
transformations in organic synthetic chemistry and the use of oxone as an efficient and mild oxidant has grown rapidly. Borhan and coworkers[14] reported a highly efficient, mild and simple protocol for the oxidation of aldehydes to carboxylic acids using oxone as the sole oxidant. Thottumkara *et al.*[15] have also reported the use of o-iodoxybenzoic acid (IBX) as a catalyst in the presence of oxone as a co-oxidant for the oxidation of primary and secondary alcohols in acetonitrile/water mixture. Herein, we wish to report ruthenium catalyzed efficient oxidation method for conversion of primary and secondary alcohols to their corresponding carboxylic acids and ketones using oxone as a co-oxidant.

Materials and Methods

IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer using TMS as internal reference. Chemical shifts for ^{1}H NMR spectra are reported (in parts per million) relative to internal tetramethylsilane (Me_4Si = 0.0 ppm) with $CDCl_3$ and $(CD_3)_2SO$ as solvents. ^{13}CNMR spectra were recorded at 100 MHz. Chemical shifts for ^{13}CNMR spectra are reported (in parts per million) relative to internal tetramethylsilane (Me_4Si = 0.0 ppm) with $CDCl_3$ and $(CD_3)_2SO$ as solvents. ^{1}HNMR data are reported in the order of chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, and m = multiplet), number of protons, and coupling constant in hertz (Hz). Silica gel G and silica gel 60-120 mesh (E. Merck) was used for thin-layer chromatography (TLC) and column chromatography respectively. TLC plates were visualized by UV or by immersion in anisaldehyde stain (by volume: 95% ethanol, 3.5% sulfuric acid, 1% acetic acid and 2.5 % anisaldehyde) followed by heating. Distilled, deionized water was used to prepare all aqueous solutions. Organic solutions of products were dried over anhydrous Na_2SO_4. $RuCl_3$, oxone and CH_3CN were purchased from Sigma-Aldrich. The starting materials in Table 2 were either purchase from HiMedia or synthesized in the laboratory and were fully characterized by IR, ^{1}H and ^{13}C NMR and MS data.

Results and Discussion

Initially, 1-octanol (1 mmol) was dissolved in CH_3CN/H_2O (9:1) mixture and to it 2 equivalent of oxone was added followed by 3 mol% of $RuCl_3$. The reaction mixture was stirred at 70°C for 5 hours during which the starting material was completely converted to the acid. The solvents were evaporated in vacuum and the compound was extracted with ethyl acetate, washed with saturated $NaHCO_3$, then with water, dried ($NaSO_4$) and concentrated to give the crude product which was finally purified by column chromatography (ethyl acetate: hexane).



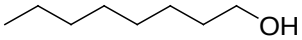
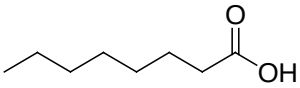
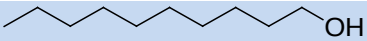
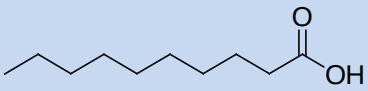
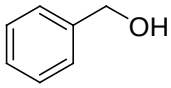
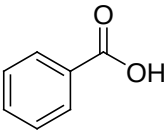
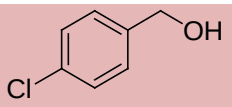
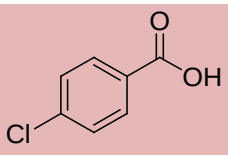
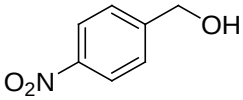
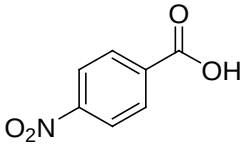
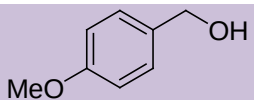
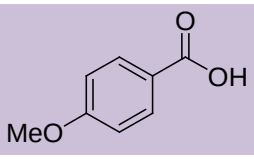
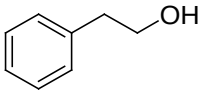
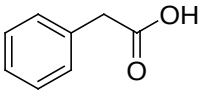
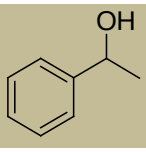
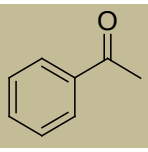
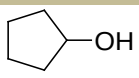
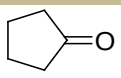
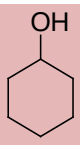
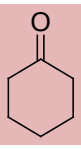
Scheme 1. Oxidation of 1-octanol.

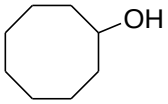
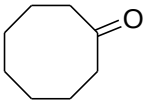
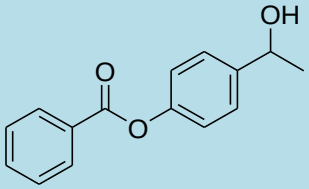
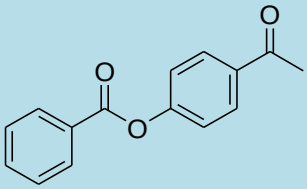
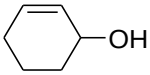
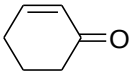
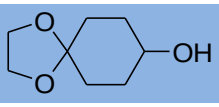
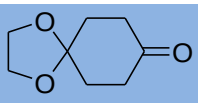
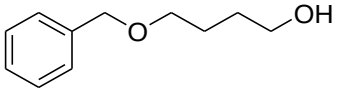
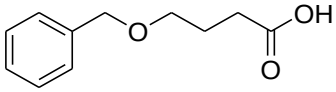
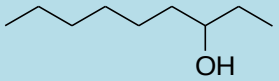
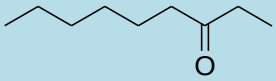
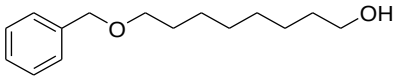
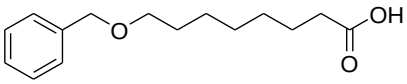
Table 1. Oxidation of 1-octanol to octanoic acid[a].

Entry	Catalyst (mol%)	Oxone® (equiv)	Unreacted Alcohols, %	Yield, % (R=OH)	Yield, % (R=H)
1	0.1	1.5	43	18	29
2	0.5	2.5	19	44	23
3	1.0	2.5	0	57	14
4	2.0	1.5	6	53	22
5	2.0	2.0	0	61	18
6	2.0	2.5	0	69	7
7	3.0	1.5	Trace	75	15
8	3.0	2.0	0	78	Trace
9	**3.0**	**2.5**	**0**	**82**	**0**
10	4.0	2.5	0	80	0
11	5.0	2.5	0	82	0

[a] All reaction are carried out at 70°C for 5 hrs.

Table 2. $RuCl_3$ catalysed oxidation of alcohols using oxone as a co-oxidant[a].

Entry	Substrate	Product	Oxone (equiv)	Time (hrs)	Yield (%)[b]
1			2.5	1.2	82
2			2.5	1.5	98
3	Docecanol	Lauric acid	2.5	12	88
4	Cetyl alcohol	Palmitic acid	2.5	12	93
5			4.0	8	81
6			4.0	7	77
7			4.0	8	73
8			4.0	8	67
9			4.0	14	71
10			2.0	1.5	77
11[c]			2.0	30 min	62
12[c]			2.0	10 min	84

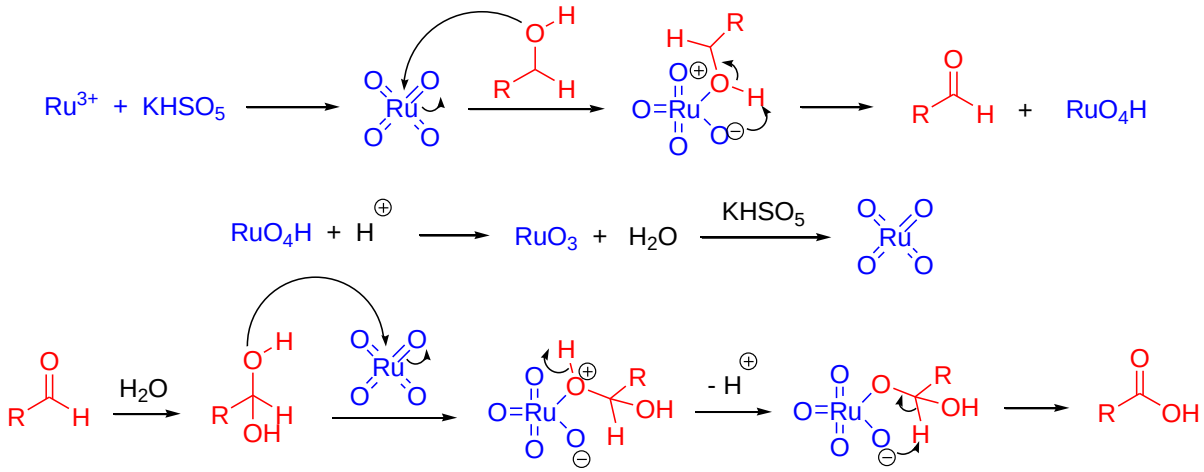
13[c]			2.0	20 min	87
14			2.0	30 min	79
15[c]			2.0	30 min	82
16[c]			2.0	30 min	87
17			4.0	4	67
18			2.0	1	81
19			4.0	4	72

[a]Unless otherwise stated, all reaction were carried out using 3 mol% $RuCl_3$, 2-4 equivalent of oxone in MeCN/H_2O mixture at 70°C, [b]Isolated yield, [c]Reaction was carried out at room temperature.

We then turned our attention to identify the minimum molar ratios of $RuCl_3$ and oxone required to effect quantitative conversion of alcohol to the corresponding carboxylic acid and the results are depicted in Table 1. We also investigated the role of temperature on the reaction. At room temperature a mixture of aldehyde and acids was obtained with aldehyde as a major product, while increasing the temperature at 50° C result in poor yield and longer reaction time. The reaction yield and time was found optimum when the temperature is maintained at 70°C and hence we optimized the yields of different products just by varying the reaction time keeping the reaction temperature at 70°C.

To test the general applicability and versatility of the method, the optimized condition was applied to various structurally diverse alcohols (Table 2). We first investigated the oxidation of primary alcohols and found that all the reaction proceeded efficiently and gave good to excellent yield (Table 2, entry 1-9, 18, 19, 21 and 22). We next examined the reactivity of secondary alcohols (Table 2, entry 10-17, 20). Oxidation of secondary alcohols also proceeded smoothly to give the corresponding ketones in nearly quantitative yields and no undesired accompaniment of Bayer-Villiger oxidation of ketones was observed. Under this reaction condition, functional groups like halo, nitro and benzoyl group are not affected and gave reasonably good yields.

It is believed that ruthenium tetraoxide formed in situ from suspension of $RuCl_3$ and oxone in a mixture of solvents is the actual oxidizing agent. As the reaction proceeds, ruthenium tetraoxide is reduced to lower valent spe-



Scheme 2. Proposed reaction mechanism.

cies. In turn, those lower valent ruthenium species are reoxidized by the cooxidant to ruthenium tetraoxide.

Conclusion

In conclusion, we developed a simple, yet efficient protocol for oxidation of primary and secondary alcohols to their corresponding carboxylic acids and ketones using oxone as a co-oxidant. We believe that the simplicity, cost-effectiveness and the use of aqueous systems as the reaction medium will make this protocol more appealing than the other methods.

General procedure for one pot conversion of alcohols to acids

To a solution of alcohols (1 mmol) dissolved in 10 mL of CH_3CN was added the required amount of an aqueous solution of oxone (1 mmol per 3mL water) followed by 3 mol% of $RuCl_3$. The reaction mixture was stirred vigorously at 70°C and the progress of the reaction was monitored by TLC. After completion of the reaction, the solvents were evaporated under vacuum and the remaining foam was dissolved in ethyl acetate (20 mL) and then washed with water (2x20 mL). The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by flash chromatography on silica gel using hexane-ethyl acetate (1:1) as elute.

Acknowledgement

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16. Selected data (Table 2):

    Entry 14: ^{1}H NMR: δ 8.15 (d, *J* = 7 Hz, 2H), 7.99 (d, *J* = 8 Hz, 2H), 7.60 (t, *J* = 8 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR: δ 196.9, 164.6, 154.6, 134.7, 133.9, 130.8, 130.2, 130.0, 129.0, 128.7, 121.9, 26.6; IR: ν (cm^{-1}) 3065, 3006, 2923, 1732, 1676, 1595.

    Entry 16: ^{1}H NMR: δ 3.95 (s, 4H), 2.42 (t, *J* = 7 Hz, 4H), 1.93 (t, *J* = 7 Hz, 4H); ^{13}C NMR: δ 209.4, 106.1, 64.0, 37.1, 32.4; IR: ν (cm^{-1}) 2953, 2923, 2854, 1705, 1097.

    Entry 17: ^{1}H NMR: δ 7.35 (s, 5H), 4.52 (s, 2H), 3.60 (t, *J* = 6 Hz, 2H), 2.34 (t, *J* = 5 Hz, 2H), 1.71 (m, 2H); ^{13}C NMR: δ 179.3, 138.9, 129.4, 129.0, 128.1, 65.2, 62.5, 32.5, 26.6; IR: ν (cm^{-1}) 3025, 2983, 2824, 2689, 1715, 1600, 1455, 1242.

    Entry 19: ^{1}H NMR: δ 7.37 (s, 5H), 4.50 (s, 2H), 3.64 (t, *J* = 6 Hz, 2H), 2.36 (t, *J* = 5 Hz, 2H), 1.62 (m, 2H), 1.53 (m, 2H), 1.35 (m, 6H); ^{13}C NMR: δ 179.4, 139.5, 129.1, 128.7, 127.8, 65.5, 63.0, 34.0, 31.6, 29.2, 29.0, 26.7, 24.5; IR: ν (cm^{-1}) 3018, 2983, 2823, 2681, 1712, 1601, 1455, 1241.