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La_2O_3 Catalyzed Oxidation of Alcohols

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Abstract

A variety of aromatic, aliphatic and conjugated alcohols were transformed to the corresponding carboxylic acids and ketones with a quantitative conversion in high yields with 70% *t*-BuOOH solution is water in the presence of catalytic amounts of La_2O_3. This method possesses a wide range of capabilities since it can be used with other functional groups which may not tolerate oxidative conditions, involves fairly simple method for work-up, exhibits chemoselectivity and proceeds under ambient conditions. The resulting products are obtained in good yields within reasonable time.

Keywords: Oxidation, Alcohol, Carboxylic Acid, La_2O_3, *t*-BuOOH

1. Introduction

The oxidation of alcohols has been of contemporary interest due to diversified potentials in organic chemistry and industrial manufacturing, and is recognized a fundamental reaction [1-5]. The oxidation of primary alcohols yields aldehydes which may be further oxidized to give carboxylic acids. The most popular and widely used reagent for oxidation is Jones reagent [6-11]. However, the reaction is stoichiometric and is performed under highly acidic conditions. Substrates having acid sensitive functionalities may not tolerate such acidity. In addition, the generation of Cr-based side products may be viewed as a potential environmental hazard [12]. Other reagents that have been used successfully include Oxone [13], calcium hypochlorite [14] and 2-hydroperoxyhexafluoro-2-propanol [15]. Excellent catalytic methods using metals have been developed using oxidation reactions. Interesting methodologies for metal mediated transformation of aldehydes to carboxylic acids have been reported recently [16-27]. The catalytic oxidation of alcohols employing transition metals such as Ru, Co, Mo, Pd, V and W have been reported [28-39]. In addition, 2,2,6,6-tetramethylpiperidinyl-1-oxyl often referred to as TEMPO along with NaClO has been an efficient combination for such oxidations [40-46]. The above reagents and methods have one or more limitations which include the use of superstoichiometric amounts of expensive reagents and use of highly basic or acidic reaction conditions. The search for catalytic processes that use environmentally benign reagents is always an attractive avenue. Our recent results highlight the oxidation of aldehydes to carboxylic acid using 30% H_2O_2 as the oxidant in the presence of catalytic amounts of $AgNO_3$ [47]. However, we were unable to convert alcohols to ketones and carboxylic acids under similar conditions. We were inspired to venture into the area of La(III) catalyzed oxidation and explore the possibility of using such compounds as catalysts for oxidation reaction.

2. Results and Discussion

We decided to explore the possibility of converting primary alcohols to carboxylic acids and secondary alcohols to ketones with the various La(III) salts. The optimization of reaction conditions for the oxidation of primary alcohols to the corresponding carboxylic acids was performed with (4-nitrophenyl)methanol as a suitable substrate in the presence of different solvents, oxidants and 5 mol% of La(III) salts (**Table 1**).

The oxidation of (4-nitrophenyl)methanol to 4-nitrobenzoic acid takes place rapidly in the presence of 5 mol% La_2O_3 and 5 equiv. 70% *t*-BuOOH (water) using MeCN as a suitable solvent (**Table 1**, Entry 1). In the presence of 2 equiv. 70% *t*-BuOOH (water), only 30% product could be isolated. With 5 equiv. 5M *t*-BuOOH (decane), the reaction was found complete in 26 h with 90% isolated yield. Various trials were done in the presence of different solvents (**Table 1**, Entries 1-9) and different La(III) salts (**Table 1**, Entries 10 and 11). Best results were obtained with 70% *t*-BuOOH (water) as the oxidant and 5 mol% of La_2O_3 as the catalyst in MeCN.

Table 1. Optimization of the reaction conditions for the conversion of (4-nitrophenyl)methanol to 4-nitrobenzoic acid with different solvents, 5 equiv. 70% *t*-BuOOH (water) and 5 mol% La(III) salts.

Entry	Catalyst	Solvent	Time (min)[a]	Yield (%)[b]
1	La_2O_3	MeCN	18	98
2	La_2O_3	EtOAc	24	75
3	La_2O_3	toluene	24	27
4	La_2O_3	CH_2Cl_2	24	71
5	La_2O_3	DMF	24	42
6	La_2O_3	DMSO	24	82
7	La_2O_3	THF	24	25
8	La_2O_3	EtOH	24	5
9	La_2O_3	$MeNO_2$	24	88
10	$LaCl_3$	MeCN	24	65
11	$LaBr_3$	MeCN	24	52

[a]Time required for complete conversion; [b]Isolated yield after column chromatography of the crude product with ethyl acetate and hexane.

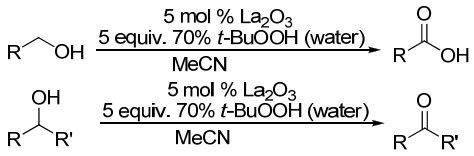
We proceeded with investigation the oxidation of various aromatic and aliphatic substrates (Scheme 1, **Table 2**).

Again we see that La_2O_3 actively catalyzes the transformation of different primary alcohols to the corresponding benzoic acid with variety of different substrates. Substitutions at different positions on the phenyl ring do not hinder the reaction, although the reaction time is affected. Our catalyst shows sufficient selectivity in this oxidation without disturbing functional groups like phenol and amine (**Table 2**, Entries 7 and 8). Oxidation of α, β unsaturated derivatives (**Table 2**, Entry 15) resulted in the formation of the expected acid in good yield. In addition, the transformation of secondary alcohols to ketones is extremely facile as indicated by Entries 17-20 of **Table 2**.

It is pertinent to mention here that mild halogenic oxidants like hypochlorites [14,48,49], chlorites [50,51] and NBS [52,53] are not suitable for substrates with electron rich aromatic rings, olefinic bonds and secondary hydroxyl groups.

The kinetic studies of the oxidation with (4-methoxyphenyl)methanol and (3-nitrophenyl)methanol were explored next. High-pressure liquid chromatography (HPLC) was used to determine the various starting materials, products and aldehyde intermediates for alcohol oxidation present as a function of time. The concentration of reactant, intermediate and product for the oxidation of (4-methoxyphenyl)methanol is shown in **Figure 1**.

The concentration of the alcohol decreases steadily while that of the carboxylic acid increases. The concentration of the intermediate aldehyde increases, achieves a steady state and then progressively converts itself to the acid. The curve showing (4-methoxyphenyl)methanol is zero-order in substrate. We have calculated the rate of such reactions. As an example let us consider the conversion of (4-methoxyphenyl)methanol to 4-Methoxybenzoic acid. The Van't Hoff differential method was used to determine the order (n) and rate constant (k) (**Figure 2**).



Scheme 1. La_2O_3 catalyzed oxidation of alcohols.

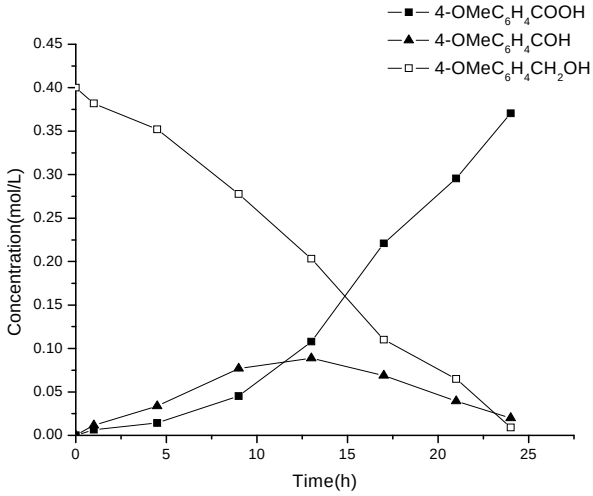


Figure 1. Van't Hoff differential plot for the oxidation of (4-methoxyphenyl)methanol with 5 mol% La_2O_3 and 5 equiv. 70% *t*-BuOOH in MeCN under ambient condition.

From **Figure 1**, the rate of the reaction at different concentrations can be estimated by evaluating the slope of the tangent at each point on the curve corresponding to that of 4-Methoxybenzylalcohol. With these data, $\log_{10}$(rate) versus $\log_{10}$(concentration) is plotted. The order (n) and rate constant (k) is given by the slope of the line and its intercept on the $\log_{10}$(rate) axis. From **Figure 2** it is clear that this reaction proceeds with second-order kinetics (n = 2.01) and the rate constant $k = 9.29 \times 10^{-1}$ $L{\cdot}mol^{-1}{\cdot}h^{-1}$. For the other substrate namely (3-nitrophenyl)methanol, the order of the reaction n = 2.02 with rate constants (k) 1.61×10^{-4} $L{\cdot}mol^{-1}{\cdot}h^{-1}$ respectively (see supporting information for details).

3. Conclusions

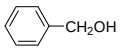
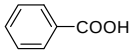
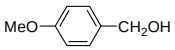
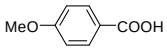
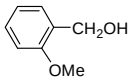
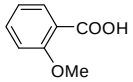
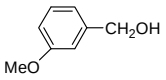
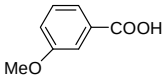
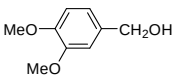
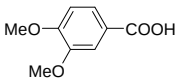
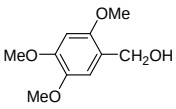
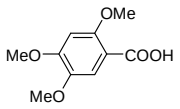
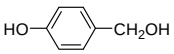
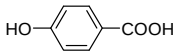
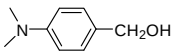
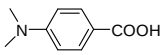
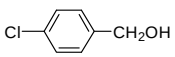
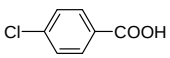
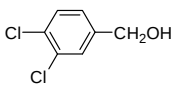
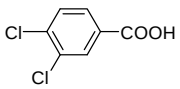
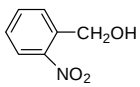
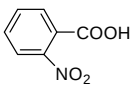
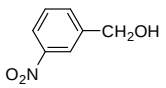
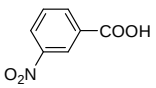
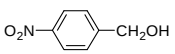
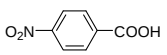
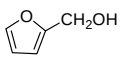
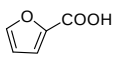
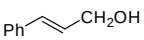
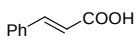
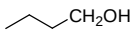
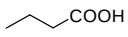
In summary, we have developed a simple, efficient, chemoselective and inexpensive catalytic method for the oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones using a table top reagent such as La_2O_3. It is noteworthy that this method does not use ligands and other additives.

4. Experimental Section

4.1. General Reagents and Equipments

All the substrates along with *t*-BuOOH, used in this

Table 2. La_2O_3 catalyzed oxidation of alcohols[a].

Entry	Alcohol	Product	Time (h)[b]	Yield (%)[c]
1			10	88
2			23	90
3			12	96
4			15	87
5			17	89
6			25	90
7			27	87
8			33	85
9			25	88
10			28	86
11			40	82
12			48	85
13			18	98
14			25	89
15			25	87
16			55	83
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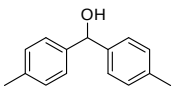
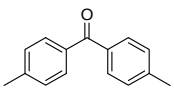
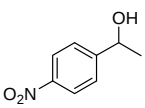
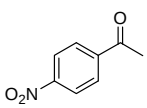
19			4	92
20			22	89

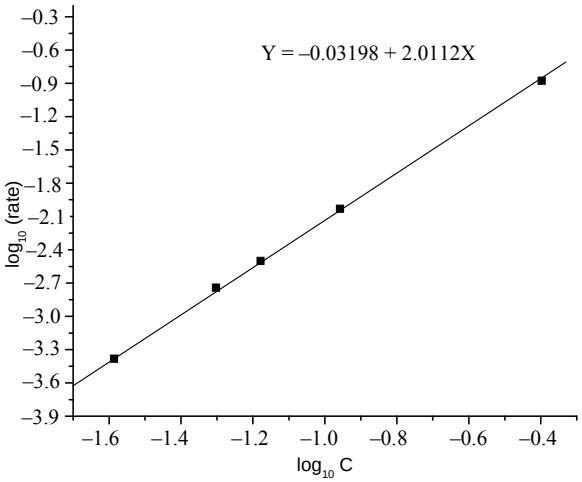


Figure 2. Van't Hoff differential plot for the oxidation of (4-methoxyphenyl)methanol with 5 mol% La_2O_3 and 5 equiv. 70% *t*-BuOOH in MeCN under ambient condition.

study were purchased from Aldrich and used as received. The solvents used were purchased from Ranchem, India and purified using standard methods. ^1H and ^{13}C spectra were recorded with a Bruker Avance 400 instrument. Chemical shifts were referenced to residual solvent resonances and are reported as parts per million relative to $SiMe_4$. $CDCl_3$ was used for NMR spectral measurements. HPLC analysis was done with Waters HPLC instrument fitted with Waters 515 pump and Waters 2487 dual λ absorbance detector.

4.2. Typical Procedure for the Oxidation of Primary Alcohol to Carboxylic Acid in MeCN

Under a nitrogen atmosphere, to a stirred solution of La_2O_3 (16.29 mg, 0.05 mmol) and primary alcohol (1 mmol) in 2.5 mL MeCN was added 70% *t*-BuOOH (water) (0.64 mL, 5 mmol). The progress of the reaction was monitored using TLC until all the alcohol was consumed. All the volatiles were removed using a rotary evaporator. The crude product was treated with saturated $NaHCO_3$ solution. This was extracted with ethyl acetate. Finally, the aqueous layer was acidified using 2N HCl and extracted with ethyl acetate. The organic layer was concentrated in vacuum and subjected to column chromatography with ethyl acetate and hexane. The spectral data of the various carboxylic acids were found to match satisfactory in accord with the literature.

4.3. Typical Procedure for the Oxidation of Secondary Alcohol to Ketone in MeCN

Under a nitrogen atmosphere, to a stirred solution of La_2O_3 (16.29 mg, 0.05 mmol) and secondary alcohol (1 mmol) in 2.5 mL MeCN was added 70% *t*-BuOOH (water) (0.64 mL, 5 mmol). The progress of the reaction was monitored using TLC until all the ketone was found consumed. All the volatiles were removed using a rotary evaporator. The residue was quenched with 2 mL water and extracted with ethyl acetate. The organic layer was concentrated in vacuum and subjected to column chromatography with ethyl acetate and hexane. Spectral characterization of the various ketones was found to match with the literature.

5. Acknowledgements

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6. Electronic Supplementary Material

The online version of this article contains supplementary material

7. References

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