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An efficient and sustainable protocol for oxidation of alcohols to carbonyl compounds

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ABSTRACT

A simple and extremely efficient protocol is developed for oxidation of alcohols to carbonyl compounds at room temperature by using green solvent lactic acid and green oxidant H_2O_2. This protocol provides high conversion under catalyst free conditions. The easy work up procedure allows high selectivity and good to excellent yields of carbonyl compounds with purity. We have performed wide range of substrates in present study with primary focus on reusability of lactic acid.

During the past decades, a great deal of attention has been given on developing new synthetic green strategies for industrial applications with respect to oxidation of organic compounds. Carbonyl compounds are very important in terms of synthetic aspect for several industries [1–4]. Synthesis of benzaldehyde is essential and plays a vital role in perfumery, dye and agro industries [5]. Therefore, the synthesis of carbonyl compounds is of great importance and attracts the attention of chemists because oxidation of alcohol is the simplest preparation route for it. Various reports are available in the literature for this course of oxidation. When catalyst free conditions are not useful for completion of the oxidation reactions then chemists move towards with homogenous [6,7] as well as heterogeneous [8,9] catalyst systems. Even though catalytic method provides convenient approach for oxidation however considering limitations make the process uneconomical [10,12]. Various protocols using Pt [13], Ru [14], Mo [15] and Cu [16] were also reported in literature. DMSO was used as activating agent for oxidation of alcohol to carbonyl compounds [17].

Oxidizing agent such as solid sodium permanganate and chromium trioxide are also used for this synthesis [18,19]. Use of peroxides such as H_2O_2 and TBHP worked well for this transformation [20–24]. The use of molecular oxygen was also helpful for this oxidation [25]. The oxidation was also carried out by using bases or alkali and also in ionic liquid [26–29]. Sonochemical oxidation of benzyl alcohol in $FeCl_3/HNO_3$ system was also reported [30]. Sodium hypochlorite pentahydrate (crystal) was used to convert alcohols to carbonyl compounds [31]. Electrochemical oxidation of alcohol could be achieved using sodium nitrite mediator in biphasic medium [32]. Although these types of traditional protocols offer satisfying yield of products, certain restrictions such as high reaction temperature or pressure, cost and toxicity of catalyst, poor biodegrability, use of unsafe reagents and lengthy reaction time prove unhealthy for environment. Hence an effective approach must be regularized for oxidation of alcohols which is profitable and free from above drawbacks.

In recent times, we have developed few eco-friendly and highly efficient protocols in our lab for oxidation of organic compounds. Green solvents have attracted chemists in the last few years as they control pollution in environment. These solvents play a vital role in green chemistry owing to their biodegradability, nontoxicity and low cost. In this context, we have used lactic acid as an effective bio based green solvent for this oxidation. Lactic acid is produced naturally as well as synthetically. Lactic acid is produced industrially by bacterial fermentation of carbohydrates [33]. It is also found primarily in sour milk products such as yogurt and some cottage cheese. It was used in several organic processes due to its nontoxic and odourless properties [34,35]. Furthermore, we use green oxidant such as H_2O_2 which is cheap and produce only water as a byproduct during oxidation. Thus in association with of our previous work [36,37], herein we wish to report efficient and selective oxidation of alcohols to carbonyl compounds in lactic acid as a solvent in presence of H_2O_2 as an oxidant at room temperature.

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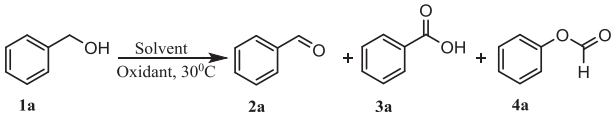
With an intention to find out the exact outcome for oxidation of alcohol to carbonyl compounds, we carried out oxidation of benzyl alcohol **1a** as an important substrate under various reaction conditions. Different reaction parameters for oxidation of **1a** (1 mmol) with lactic acid (1 mL) as a solvent and 30% H_2O_2 as an oxidant at room temperature were optimized (Table 1). During this study, initially we carried out the oxidation of **1a** using lactic acid in the absence of oxidant H_2O_2 at room temperature. It has been observed that there was no conversion up to 8 h (Table 1, entry 1). Next, we added H_2O_2 (1 equiv.) in to the mixture of **1a** and lactic acid and found 72% conversion of reaction mixture after 7 h (Table 1, entry 2). Increasing the amount of H_2O_2 from 1 to 1.03 and 1.06 equiv. and conversion also increased from 89% to 95% respectively (Table 1, entry 3,4). When conc. of H_2O_2 was increased to 1.07 equiv. in to mixture of **1a** and lactic acid, 100% conversion of **1a** was observed with formation of the desired product selectively benzaldehyde **2a** 99.6% with slight impurity formation benzoic acid **3a** 0.1% and phenyl formate **4a** 0.3% in 7 h (Table 1, entry 5). With further increase in the amount of H_2O_2 from 1.07 to 1.10 equiv. it was observed that selectivity of **2a** decreases with increase in selectivity of **3a** and **4a** (Table 1, entry 6). This oxidant equivalent study indicates that H_2O_2 is the key oxidant for proper transformation and 1.07 equiv. is suitable for maximum conversion and excellent selectivity of **2a**.

Subsequently, we checked out the solvent effects on oxidation of **1a** in to **2a** (Table 1, entry 7–14). Solvent less reaction mixture gave only 9% conversion of **1a** in to **2a** (Table 1, entry 7). Several polar and non-polar solvents were also tested for this oxidation. We carried out the oxidation of **1a** in to **2a** using polar aprotic solvents, 48% and 42% conversion of **1a** to **2a** was observed with acetonitrile (MeCN) and acetone respectively (Table 2, entry 8–9) while using ethyl acetate (EtOAC) only 38% conversion was obtained (Table 1, entry 12). It was observed that oxidation of **1a** in polar protic solvents like methanol (MeOH) and water gave 55% and 46% conversion in 7 h respectively (Table 1, entry 10–11). Moreover, we performed this oxidation in non-polar solvents such as hexane and chloroform ($CHCl_3$) and obtained less conversion of **1a** in to **2a** (Table 1, entry 13–14). This above solvent study showed that bio based lactic acid is the best solvent for the complete conversion of **1a** in to **2a**.

Next, we carried out the comparison study with different oxidants on oxidation of **1a** to **2a** (Table 2). Oxidizing agents such

Table 1
Optimization of reaction parameters.[a]



1a **2a** **3a** **4a**

Entry	Solvent	Oxidant (equiv.)	Time (h)	Conv.[b] (%)	Sel.[b] (%)		
					2a	**3a**	**4a**
Oxidant eqiv. Study							
1	Lactic acid	–	8	–	–	–	–
2		1.00	7	72	72	0	0
3		1.03	7	89	89	0	0
4		1.06	7	95	94.8	0.1	0.1
5		**1.07**	**7**	**100**	**99.6**	**0.1**	**0.3**
6		1.10	7	100	97	1.2	1.8
Solvent study							
7	–	1.07	8	09	08	1	0
8	MeCN		7	48	47	1	0
9	Acetone		7	42	41	1	0
10	MeOH		7	55	52	3	0
11	H_2O		8	46	44	2	0
12	EtOAc		7	38	38	0	0
13	Hexane		7	35	34	1	0
14	$CHCl_3$		7	22	20	2	0

[a] Reaction conditions: **1a** (1 mmol), Solvent (1 mL), 30% H_2O_2 (equiv.), temperature (30 °C).
[b] conversion and selectivity determined by GC with the area normalization method.

Table 2
[a]Comparison with different oxidants and temperature.

Entry	Oxidants (equiv.)	Temp. (°C)	Conv.[b] (%)	Sele.[b] (%)		
				2a	**3a**	**4a**
Oxidants study						
1	m-CPBA	30	77	75	0.8	12
2	70% TBHP		66	63	1.3	1.7
3	Benzoyl peroxide		58	55	0.5	3.5
4	UHP		50	49	0.2	0.8
Temperature study						
5	H_2O_2	15	43	43	0	0
6		20	61	61	0	0
7		25	89	88.9	0	0.1
8		35	100	99.4	0.2	0.4

[a] Reaction conditions: **1a** (1 mmol), Lactic acid (1 mL), oxidants (1.07 equiv.), Time (7 h), temperature (°C),
[b] conversion and selectivity determined by GC with the area normalization method.