



SELECTIVE OXIDATION OF ALCOHOLS TO ALDEHYDES BY USING HYDROGEN PEROXIDE AS AN OXIDANT: A REVIEW

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ABSTRACT

The oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both at a laboratory and industrial scale. The transformation of alcohols into aldehydes or ketones is a fundamental reaction in organic synthesis, a number of methods are known for alcohol oxidation, and however the development of newer methods and methodologies is gaining much attention currently due to the significance of this reaction. . The utilization of the hydrogen peroxide as an oxidant for organic substrates has gained much attention in recent years, because of its environmental implications, water being the only chemical by-product; on the other hand, the water is actually used as process solvent, so the reactions are of general interest due to their potential in combinational chemistry, simple processes, easy work-up, low cost and reduction in noxious waste materials. This review mainly focuses on the selective oxidation of alcohols to aldehydes by using hydrogen peroxide as an oxidant.

Keywords: Alcohols, Aldehydes, Environmentally Safe Oxidation, Hydrogen Peroxide, Selective oxidation.

I. INTRODUCTION

The oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both at a laboratory and industrial scale [1]. Also the oxidation yielding ketones and aldehydes is a chemical transformation of primary industrial importance in fine chemistry, carbonyl compounds being precursors of a variety of valuable fine chemicals including drugs, vitamins and fragrances [2]. The catalytic conversion of primary and secondary alcohols into their corresponding aldehydes and ketones is an essential reaction in organic synthesis [3, 4]. The catalytic oxidation with hydrogen peroxide in aqueous solutions offers an economic and environmentally safe alternative for oxidation reactions performed in synthetic laboratories and chemical industry. Applications where oxidation reactions are required are diverse, ranging from pulp and textile bleaching to production of fine chemicals. At the moment, most of these processes are carried out by using stoichiometric oxidants, such as peroxides, chlorine-bearing compounds and high valent transition metal oxides.

The transformation of alcohols into aldehydes or ketones is a fundamental reaction in organic synthesis [5], a number of methods are known for alcohol oxidation, and however the development of newer methods and methodologies is gaining much attention currently due to the significance of this reaction. Alcohol oxidation reactions with stoichiometric amounts of bichromate and permanganate of the previous century are being replaced by modern methods involving catalytic amounts of metal catalysts in combination with oxidants such as dioxygen or hydrogen peroxide. In the last four years some fine articles have appeared, describing manganese [6], copper [7, 8], ruthenium [9, 10], iron [11], palladium [12, 13], gold [14, 15] catalyzed reactions with dioxygen or hydrogen peroxide. The utilization of the hydrogen peroxide as an oxidant for organic substrates has gained much attention in recent years, because of its environmental implications, water being the only chemical by-product; on the other hand, the water is actually used as process solvent, so the reactions are of general interest due to their potential in combinational chemistry, simple processes, easy work-up, low cost and reduction in noxious waste materials. A series of catalytic systems for the hydrogen peroxide-based oxidation of alcohols to aldehydes have been reported [16, 17].

II. OXIDATION OF ALCOHOL TO ALDEHYDES BY USING HYDROGEN PEROXIDE (H₂O₂) AS AN OXIDANT

Ankush V. Biradar et al., studied the selective oxidation of various aromatic alcohols to aldehydes. In that work very high conversion (90%) and selectivity (90%) for aldehydes were achieved by using cyclopentadienyl molybdenum acetylide complex, CpMo (CO)₃(C, CPh) (1) as catalyst and hydrogen peroxide as environmentally benign oxidant. Water soluble Mo acetylido-oxo-peroxo species is formed in situ after reaction of the complex with aqueous hydrogen peroxide during the course of reaction as catalytically active species. Interestingly even though the catalyst is homogeneous it could be recycled very easily by separating the products in organic phase and catalyst in aqueous phase using separating funnel. Even after five recycles no appreciable loss in alcohol conversion and aldehyde selectivity was observed. The percentage of conversion and selectivity is reported by them is shown in Table 1 [18].

Feng Shi et al., worked on selective oxidations of alcohols and olefins with hydrogen peroxide and found that catalyst activity and selectivity are controlled by tuning the particle size. The formation of a thin carbon-layer on the surface of the nano-iron oxide during the reaction permits for high catalyst stability high selectivity with acceptable activity was achieved by tuning the particle size of nano iron oxide into the range of 20–50 nm. The results reported by them are tabulated in Table 2. [19]

M.G. Buonomenna et al., has their research based on selective oxidation of benzyl alcohols to aldehydes by PEEKWC microcapsulation. In their work, PEEKWC catalytic microcapsules have been used as heterogeneous catalyst and interphase contactor in oxidation of benzyl alcohols to benzaldehydes. Substituted benzyl alcohols can be oxidized selectively to corresponding benzaldehydes with hydrogen peroxide as oxidizing agent and ammonium molybdate as catalyst entrapped in the polymeric microcapsules (Table 3). [20]

Nan Jiang and Arthur J. Ragauskas studied TEMPO-catalyzed oxidation of benzylic alcohols to aldehydes with the H₂O₂/HBr/ionic liquid [bmim] PF₆ system. They found that a selective oxidation of benzylic alcohols to the corresponding aldehydes in room temperature ionic liquid was achieved by using TEMPO/HBr/H₂O₂ system,

and both ether-insoluble acetamido-TEMPO and ionic liquid [bmim] PF₆ can be successfully recovered and reused for the oxidation of the same (different) substrate as shown in Table 4 [21].

Unnikrishnan R. Pillai and Endalkachew Sahle-Demessie had studied the selective oxidation of alcohols over vanadium phosphorus oxide catalyst using hydrogen peroxide. They found that the catalyst and the method are found to be suitable for the selective oxidation of a variety of secondary aliphatic, alicyclic and aromatic alcohols to the corresponding ketones. The catalyst is soluble in the reaction mixture; however, it could be reused by the addition of new batch of substrate along with the solvent and oxidant to the previous reaction mixture. The reaction mechanism is expected to involve a redox cycle in which V⁴⁺ in combination with dynamic V⁵⁺ sites are acting as the active centers. The active V⁴⁺ phase is expected to be a vanadium complex with oxo and phospho ligands. The results were reported in Table 5 [22].

Junhua Liu et al. had studied oxidation of alcohols to aldehydes with hydrogen peroxide catalyzed by Pd (OAc)₂/SO under solvent-free conditions. They concluded that secondary and primary aliphatic alcohols, primary allylic alcohols could be efficiently oxidized to aldehydes or ketones in high yields in the presence of Pd (OAc)₂ sodium oxalate (SO) under solvent-free conditions, it is a high yielding and operationally simple method. Acetic acid is testified to attend the reaction, the acetate ligands are envisioned to serve two purposes: as a ligand for the Pd^{II} center and as a base to deprotonate the Pd-bound alcohol, but acetic acid has not shown in previous bidentate ligands systems, so a mechanism is proposed on the basis of the mechanisms reported by the pioneers. The results are shown in Table 6. The reaction conditions are Pd (OAc)₂/SO 17.9 mg (0.05 mmol), alcohol (10 mmol), hydrogen peroxide (5 ml), 70°C for 8 h [23].

Sandro Campestrini et al. reported alcohol oxidation with hydrogen peroxide promoted by TPAP-doped ormosils, they have discovered that TPAP-doped organically modified silica gels are effective catalysts for the oxidation of alcohols by hydrogen peroxide at room temperature, provided that the oxidant solution is added slowly. The effect of surface catalyst hydrophobicity is opposite of that found in aerobic alcohols oxidation and is consistent with the polar nature of the H₂O₂ primary oxidant (Table 7). Considering the ease of exploiting hydrogen peroxide formed in situ¹⁷ and the unique advantages of commercial sol gel catalytic materials, ²⁰ these findings might open the way to the introduction of environmentally friendly and cost-effective alcohols oxidation. The reaction conditions are (0.05mmol in 3.0mL of ether) with hydrogen peroxide (3.0mL of H₂O₂ 0.047 M in ether added at the velocity of 0.15mL/h) catalysed by TPAP (0.0025mmol) encapsulated in various MTMS/TMOS mixed gels, in the presence of 3A ° molecular sieves, at 25°C [24].

Jelle Brinksma et al. in their research studied that in situ prepared manganese complexes based on ligands 1-6 have been used in the catalytic oxidation of alcohols to aldehydes or ketones. Highly active and selective catalysts were found with excellent turnover numbers (up to 900) using aqueous hydrogen peroxide as oxidant at ambient temperatures. EPR spectroscopy and electrospray mass spectrometry has indicated that dinuclear species may be involved in the catalytic oxidations. Comparing the rate of oxidation of benzyl-d₇ alcohol with that of benzyl alcohol by the different catalysts yielded isotope effects (k_H/k_D) of 2.2- 4.3. Although the exact nature of the oxidising species has not been elucidated, these results (Table 8) indicate that hydroxyl radicals are not involved in these processes. The experiments were carried out with different ligands and the samples were analyzed by GC (HP 6890, column HP1 15-0.3 mm-2.65 mm, polydimethylsiloxane) [25].



Takemasa Hida and Hideo Nogusa reported oxidation of alcohol using novel $\text{Na}_2\text{WO}_4\text{-H}_2\text{O}_2$ system under neutral conditions. The oxidation of alcohol to ketone or aldehyde was carried out by using N, N dimethylacetamide, hydrogen peroxide, and a catalytic amount of disodium tungstate dihydrate under neutral conditions. This method is very simple, practical for large scale manufacturing, and applicable to a variety of substrates including an acid-sensitive substrate. Disodium tetraperoxotungstate dihydrate ($\text{Na}_2 [\text{W}(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$) was isolated from a mixture of N,N-dimethylacetamide, hydrogen peroxide, and disodium tungstate dihydrate, and a proposal reaction mechanism is discussed in the paper. The results were tabulated in Table 9 [26].

A clean catalytic process for the synthesis of benzaldehyde (BzH), with high selectivity, from benzyl alcohol (BzOH) by oxidation with hydrogen peroxide (H_2O_2), without any organic solvent in a batch reactor was studied by Manisha P. Chaudhari, Sudhirprakash B. Sawant. Oxidation of BzOH to BzH was carried out at different speeds of agitation (800–1500 rpm), temperatures (343–363 K), catalyst loadings $((3.4\text{--}5.9) \times 10^{-3} \text{ mol/L})$ and mole ratios of BzOH: H_2O_2 (1:1–1:2). Effect of various catalysts, e.g. tungstic acid, ammonium molybdate, and sodium tungstate and sodium molybdate on the oxidation of BzOH to BzH was studied. Ammonium molybdate was found to be the best catalyst for the oxidation of BzOH as compared to other catalysts. Increasing the speed of agitation beyond 1000 rpm has no significant effect on the rate of the oxidation of BzOH, indicating the absence of mass transfer resistance. BzOH can be oxidized selectively to benzaldehyde, with hydrogen peroxide as an oxidizing agent and ammonium molybdate and tungstic acid as catalysts. The conversion of BzOH increases with increase in the catalyst concentration. Amongst the catalysts used, ammonium molybdate was found to be the best catalyst for oxidation of BzOH by H_2O_2 . The rate of reaction increases with increase in the reaction temperature. The reaction shows first-order dependence on the concentration of BzOH and the catalyst. The rate constant, k , observed to be 2.5 times more for ammonium molybdate compared with tungstic acid. Values of activation energy for oxidation of BzOH are as 84 and 96 kJ/mol for ammonium molybdate and tungstic acid, respectively [27].

Wolfgang A. Herrmann et al. found that a four-component system (H_2O_2 , MTO, HBr, TEMPO) in acetic acid catalyzes the selective oxidation of terminal alcohols to the corresponding aldehydes with excellent selectivity and yield (table 10). The system allows the oxidation of alcohols with hydrogen peroxide as oxidants either selectively to aldehydes or to the corresponding acids, depending on the reaction parameters. The new technique is especially applicable to the oxidation of carbohydrates. The four-component system MTO, H_2O_2 , HBr and TEMPO in acetic acid is efficient for the selective catalytic oxidation of terminal alcohols. An important advantage apart from the accessibility, the mild conditions, and the short reaction times is the amazing highly selective formation of aldehydes. They succeeded in the desired substitution of bleach (NaOCl) as primary oxidant by the application of environmental friendly hydrogen peroxide in BrO:TEMPO mediated oxidation reactions. Furthermore, the catalytic system (MTO, H_2O_2 , HBr) without TEMPO allows oxidation of the C₆-atom to the corresponding carboxylic acid of carbohydrates as demonstrated for starch. The MTO based oxidation of terminal alcohol groups in carbohydrates opens perspectives for broadly desired industrial applications in this area [28].



III. CONCLUSION

The review has attempted to cover most of the selective oxidation of alcohols to aldehydes mainly by hydrogen peroxide as an oxidant. The utilization of the hydrogen peroxide as an oxidant for organic substrates which acquires advantages such as environmental implications, water being the only chemical by-product, simple processes, low cost and reduction in lethal waste materials. As Hydrogen peroxide (H_2O_2) is a clean and environment friendly reagent which has widespread use in the oxidation of organic compounds. Thus it is one of clean and environment friendly oxidation process with higher yield in the selective oxidation of alcohols to aldehydes.

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Table 1: Oxidation of Different Alcohols [18]

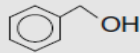
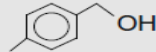
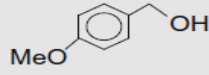
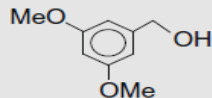
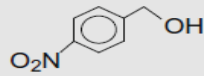
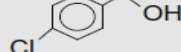
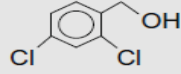
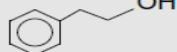
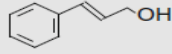
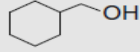
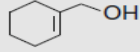
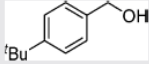
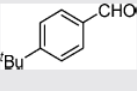
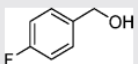
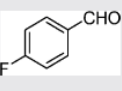
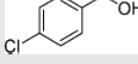
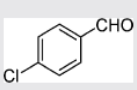
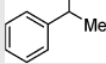
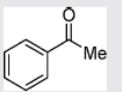
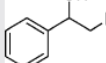
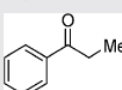
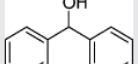
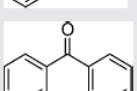
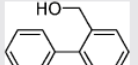
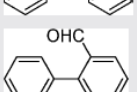
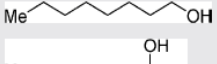
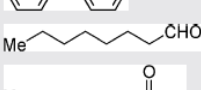
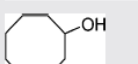
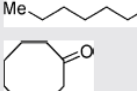
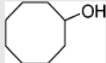
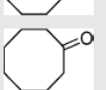
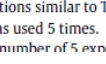
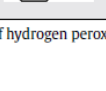
Entry	Substrate	% conv	Selectivity (%)		TON	Yield (%)
			Aldehyde	Acid		
1		86	92	8	396	79
2		90	87	13	391	78
3		90	90	10	392	90
4		83	85	15	352	71
5		60	88	12	264	53
6		65	91	9	296	62
7		78	90	10	343	70
8		72	82	18	295	59
9		70	75	25	262	52
10		82	88	12	361	72
11		82	85	15	348	68

Table 2: Selective Oxidation of Alcohols to Aldehydes and Ketones with Nano-Fe₂O₃[19]

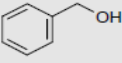

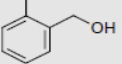

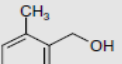

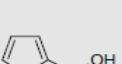

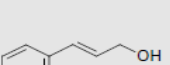
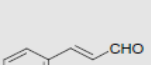
Entry	Substrate	Product	Conversion (%)	Selectivity (%)	TON
1			10	>99	10
2			87	51	44
3			98	61	60
4			42	60	25
5			35	42	44
6			49	52	25
7			6	>99	6
8			-	-	-
9			6	>99	6
10			14	>99	14
11 ^b			15	>99	70 ^c

^a Reaction conditions similar to Table 1, except that 1.5 equiv. of hydrogen peroxide is used.

^b The catalyst was used 5 times.

^c Total turnover number of 5 experiments

Table 3: Oxidation of Alcohols by the Catalytic Microcapsules PEEKWC-Mo₇ and with the Homogeneous Catalyst (NH₄)₆Mo₇O₂₄ · 4H₂O (Mo₇) [20]

Entry #	Substrate	Product	Catalyst	Conversion (%)	Selectivity ^a (%)
1			Mo ₇	22.5	97
			PEEKWC-Mo ₇	26.7	99
2			Mo ₇	24.3	95
			PEEKWC-Mo ₇	10.8	97
3			Mo ₇	18	97
			PEEKWC-Mo ₇	16	99
4			Mo ₇	50	17.2
			PEEKWC-Mo ₇	6.9	31
5			Mo ₇	86.4	100
			PEEKWC-Mo ₇	77.0	100

**Table 4: Oxidation of Alcohols to Aldehydes in [bmim] PF₆[21]**

Entry	Benzylic alcohols	Condition	Products	Yields (%) ^b
1		2 equiv H ₂ O ₂ , 2 h		92
2		2 equiv H ₂ O ₂ , 3 h		83
3		2 equiv H ₂ O ₂ , 3 h		81
4		2 equiv H ₂ O ₂ , 2 h		87
5		3 equiv H ₂ O ₂ , 4 h		93
6		5 equiv H ₂ O ₂ , 4 h		72 ^c
7		3 equiv H ₂ O ₂ , 4 h		91
8		4 equiv H ₂ O ₂ , 4 h		83
9		2 equiv H ₂ O ₂ , 2 h		—

^a The reactions were carried out in 2 mmol scale at 40 °C.^b Isolated yield by flash chromatography.^c The reaction was carried out at 50 °C.**Table 5: Oxidation of Various Alcohols over VPO catalyst using H₂O₂ and Acetonitrile^a [22]**

Entry	Alcohol	Product	Conversion (%)	Selectivity (%)	TON
1	1-Pentanol	1-Pentanal	06	100	09
2	2-Pentanol	2-Pentanone	33	100	51
3	3-Pentanol	3-Pentanone	38	100	58
4	1-Hexanol	1-Hexanal	07	100	11
5	2-Hexanol	2-Hexanone	59	100	91
6	3-Hexanol	3-Hexanone	52	100	80
7	Cyclohexanol	Cyclohexanone	44	100	68
8	2-Methyl Cyclohexanol	2-Methyl Cyclohexanone	39	100	60
9	3-Methyl Cyclohexanol	3-Methyl Cyclohexanone	32	100	49
10	4-Methyl Cyclohexanol	4-Methyl Cyclohexanone	40	100	62



11	4-t butyl Cyclohexanol	4-t butyl Cyclohexanone	40	100	62
12	Cyloheptanol	Cyloheptanone	61	100	94
13	2-Octanol	2-Octanone	23	100	35
14	Exo-norborneol	Exo-norborneone	50	88 ^b	77
15	Iso-borneol	Iso-borneone	85	100	131
16	Benzhydrol	Benzhydrone	52	100	80
17	Benzyl alcohol	Benzyl alcohone	66	78 ^c	102
18	1-Phynel ethanol	1-Phynel ethanone	77	100	118
19	2-Phynel ethanol	Phynel aldehyde	10	100	15
20	2-Florobenzyl alcohol	2-Florobenzyl aldehyde	42	62 ^d	65

^a Reaction conditions : 10mmol alcohol, 10mg catalyst, 40mmol 30% H₂O₂, 10 ml acetonitrile, 65⁰C, 4h, stir, N₂

^b Remaining dinorbomanone

^c Remaining benzoic acid

^d Remaining fluoro benzoic acid TON: Trun over Number= no of moles of product formed per moles of V in the catalyst sample

Table 6: Oxidations of Alcohols with Hydrogen Peroxide Catalyzed by Pd (OAc)₂/SO Under Solvent-Free Conditions [23]



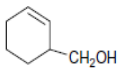
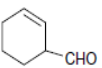
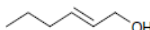
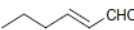
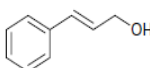
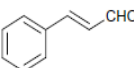
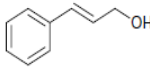
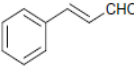
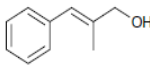
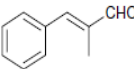
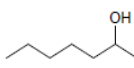
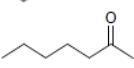
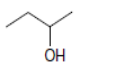
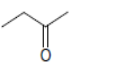
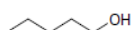



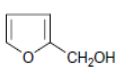
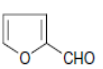
Entry	Time (h)	Substrate	Product	Conversion (%)	Yield ^b (%)
1	8			100	97
2	8			95	92
3	8			100	96
4	8			100	96
5	8			100	97
6	8			97	94
7	10			100	>99
8	8			100	>99
9	16			92	92
10	18			87	87
11	14			95	95



Table 7: Alcohol Conversion, Aldehyde and Acid Yields as Function of Catalyst Methylation in the Oxidation of Benzyl Alcohol [24]

Run	MTMS (%)	Benzyl alcohol conversion (%)	Benzaldehyde yield (%)	Benzoic acid yield (%)
8	0	93.4	86.2	7.2
9	25	90.7	82.5	8.2
10	50	82.07	63.5	19
11	75	73.1	68.5	4.6
12	100	49.3	49.3	0
13	0 ^a	99.0	72.7	26.3
14	0 ^b	94.3	94.3	0
15	100 ^a	51.2	51.2	0

^a 3.0 ml of H₂O₂ 4.7*10⁻² M in ether added at velocity of 0.04 mL/h.

^b 3.0 ml of H₂O₂ 2.3*10⁻² M in ether added at velocity of 0.15 mL/h.

Table 8: Oxidation of Selected Alcohols with in Situ Prepared Mn-Catalysts Based on Ligands 2-6 [25]

Substrate	Turnover number after 4h (ton) ^c and selectivity (%) with ligands 2-6									
	2	Selec tivity ^d	3	Selec tivity ^d	4	Selec tivity ^d	5	Selec tivity ^d	6	Selec tivity ^d
Benzyl alcohol	326	95	127	95	293	95	331	99	303	99
4- Methoxybenzyl alcohol	201	80	97	80	255	80	270	75	291	75
4-chlorobenzyl alcohol	449	99	127	99	308	99	392	99	414	99
4- Trifluoromethyl benzyl alcohol	329	70	173	90	352	90	317	70	258	70
4- Fluoromethyl benzyl alcohol	233	90	21	99	231	88	240	80	248	70
2,5-Dimethoxybenzyl alcohol	90	99	63	99	72	99	71	99	63	99
Cyclohexanol	363	95	486	80	595	70	583	85	593	80
Cycloheptanol	849	85	735	90	894	90	808	99	688	99
1-Octanol	108	85	53	85	63	70	53	90	46	90
2-Octanol	680	95	298	95	555	95	664	85	480	95
Sec pheynlethyl	657	90	400	70	593	70	793	90	715	95



alcohol										
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^b All products were identical to independent samples and identified by GC (HP 6890, column HP1 15-0.3 mm-2.65 mm, polydimethylsiloxane) and ¹H NMR.

^c Turnover number* mole product per mole ligand.

^d Selectivity in mole aldehyde (or ketone) per mole converted substrate.

Table 9: Oxidation of Several Alcohols^a [26]

Entry	Substrate	H ₂ O ₂ (equiv)	Reaction time (h)	Product	Yield of keton
1		1.2	4		91 ^b
2		1.2	1		>99 ^c
3		1.2	2		74 ^d
4		1.2	4		86 ^d
5		1.2	4		98 ^e
6		4.4	10		96 ^e
7		1.1	1		90 ^c
8		1.1	1		95 ^c
9		1.1	4		20 ^{c,f}
10		1.1	4		50 ^g

^a 35% H₂O₂, 1 mol% Na₂WO₄·2H₂O, and 4 mol% Na₂HPO₄·12H₂O in DMA at 90 °C. Concentration of substrate was 0.2 M.

^b Isolated by crystallization.

^c Determined by HPLC analysis.

^d Isolated by silica gel column chromatography.

^e Determined by GC analysis.

^f 4-Nitrobenzyl alcohol was recovered in 45% and *p*-nitrobenzoic acid was yielded in 35%, which were determined by HPLC.

^g 2-Ethyl-1-hexanol was recovered in 33%, which was determined by GC.

Table 10: MTO:HBr:TEMPO Catalyzed Oxidation of Terminal Alcohols (by GC-MS) [28]

Substrate	Time (min)	Conversion (%)	Selectivity (%)
Benzyl alcohol	1	51	>99
Benzyl alcohol	15	70	>99
Benzyl alcohol	120	81	>99
4-Isopropyl benzyl alcohol	1	62	>99
4-Isopropyl benzyl alcohol	15	78	>99
4-Isopropyl benzyl alcohol	120	>90	>99