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Efficient synthesis of carbonyl compounds: oxidation of azides and alcohols catalyzed by vanadium pentoxide in water using *tert*-butylhydroperoxide

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ABSTRACT

Catalytic amount of vanadium reagent with *tert*-butylhydroperoxide as the oxidant was found to be an excellent oxidizing agent in aqueous medium. Vanadium pentoxide with aq *tert*-butylhydroperoxide readily oxidizes primary benzylic azides to the corresponding acids and secondary benzylic azides to the corresponding ketones in excellent yields. Further, vanadium pentoxide and aq *tert*-butylhydroperoxide combination turned out to be an effective catalyst for the oxidation of alcohols. Using vanadium pentoxide and aq *tert*-butylhydroperoxide primary alcohols were oxidized to the corresponding acids, whereas secondary alcohols underwent a smooth transformation to furnish corresponding ketones in excellent yields. All the oxidations are performed in water.

1. Introduction

Synthesis of carbonyl compounds by oxidation of a variety of substrates is one of the fundamental transformations in organic synthesis, which has wide applications in academia and industry.[1] This is due to occurrence of carbonyl compounds as intermediates, and final products in several natural products, fine chemicals and medicinally important compounds.[2] Due to these reasons, a variety of oxidizing strategies are developed to accomplish carbonyl compounds and their derivatives,[1] which led to the discovery of several oxidizing agents.[3–5] However, the utility of stoichiometric amount of metal reagents for oxidation is a serious impediment as it generates toxic by-products, and need larger amount of oxidizing agents.[6] With increasing environmental concerns, there is a surge of efforts for developing environmentally benign methods for the oxidation of organic compounds.[7] Hence, one can notice a number of catalytic procedures, which employ environmentally benign oxidants, solvents and reaction conditions.[8] Catalytic oxidation in water using a variety of user-friendly oxygen sources such as O_2, H_2O_2, *tert*-butylhydroperoxide (TBHP)[9] etc. are useful on the point of view of environmental benefits.[10]

Over the years, metal catalyzed selective oxidation has witnessed an extensive development and application. Utility of vanadyl acetylacetone ($VO(acac)_2$) and TBHP system,[11–14] are the classical examples of using vanadium catalysts. Furthermore, vanadium reagents, such as $VO(acac)_2$,[15] vanadyl isopropoxide ($VO(O^iPr)_3$),[16] and vanadium pentoxide (V_2O_5)[9a,17] etc., are used in the oxidation of alcohols,[18] sulfides,[19] amines,[20] and olefins,[21] and most of these reactions are performed in conventional organic solvents. In this context, herein we report utility of vanadium pentoxide (**1**) in oxidation of organic azides as well as alcohols using water as the solvent.

2. Results and discussion

2.1. Oxidation of benzylic azides

In our earlier studies, we reported oxidation of azides and alcohols using molybdenum catalyst.[22–25] Since organic azides are used as precursor for nitriles,[26] nitro compounds,[27] aldehydes, ketones,[28] and in click chemistry,[29] there is a growing interest in studying the reactivity of azides with a variety of reagents.[30] At the same time, as molybdenum and vanadium enzymes are behaving alike in nitrogen fixation,[31–33] we thought it is appropriate to study the reactivity of vanadium reagents with azides and alcohols. Perhaps, the oxidation of organic azides is important in understanding the role of vanadium in nitrogen fixation. Apart from this, efforts directed on the functionalization of hydrocarbon via C–H bond activation has led to direct synthesis of azides from the corresponding hydrocarbons.[34] Additionally, synthesis of benzylic azides from corresponding alkyl arenes[35] has provided an access to synthesize benzylic azides without using the corresponding alcohols or

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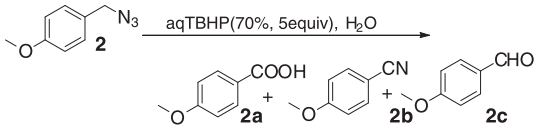
halides. Furthermore, manipulation of azides to a variety of products appear to be useful in organic synthesis. Therefore, it is important and useful to develop new methods to oxidize azides to the corresponding carbonyl compounds by user-friendly protocols. Importantly, these protocols avoid using alcohols or halides for the oxidation to produce carbonyl compounds. For the optimization studies, oxidation of *p*-methoxybenzyl azide (**2**) is studied by employing a variety of vanadium reagents and oxidants (Tables 1 and 2). As can be seen in Table 1, reaction of azide **2** with VO(acac)$_2$ (5 mol %) and TBHP in aqueous medium furnished aldehyde **2c** in 46% along with a trace amount of the corresponding acid **2a** (entry 1, Table 1). However, the same reaction under the forcing condition (100 °C) resulted in the formation of corresponding acid **2a** in 70% (entry 2, Table 1). It is noteworthy to point out that these reactions were carried out in water. However, the reaction of azide **2** with $VOSO_4 \cdot XH_2O$[36] in TBHP resulted in the formation of the corresponding acid **2a** in 64% yield (entry 3, Table 1). Furthermore, the oxidation of azide **2** with V_2O_5 and TBHP afforded the acid **2a** in 74% along with the minor amount of corresponding nitrile **2b** (12%, entry 4). However, an attempt to oxidize the azide **2** with TBHP in the absence of catalysts at reflux condition resulted in the formation of corresponding aldehyde **2c** in trace amount (entry 5, Table 1). Our attempts to obtain nitrile exclusively did not yield fruitful results.

Table 1
Oxidation of p-methoxybenzyl azide (optimization of catalyst)



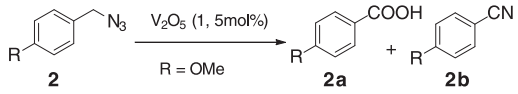
Entry	Catalysts[a]	Temp (°C)	Time (h)	Yield[b] (%)		
				2a	**2b**	**2c**
1	VO(acac)$_2$	rt	20	Trace	—	46
2	VO(acac)$_2$	100	10	70	—	—
3	$VO(SO_4) \cdot XH_2O$	rt	36	64	—	—
4	V_2O_5(**1**)	rt	36	74	12	—
5	None	100	36		—	Trace

[a] 5 mol %.
[b] Isolated yield.

With these preliminary information, oxidation of **2** was performed with V_2O_5 (**1**, 5 mol %) by employing a variety of oxygen sources and solvents (Table 2). The reaction of **2** with **1** (5 mol %) in oxygen atmosphere did not proceed to form the product either in room temperature or in the presence of several oxygen sources, such as molecular oxygen, NaOCl or $NaBO_3 \cdot H_2O$, but the starting material was recovered (entries 1–6, Table 2). Similarly, the reaction of azide **2** in the presence of aq H_2O_2 (50% solution) did not result in the formation of expected product (entry 7, Table 2). Interestingly, the same reaction of **2** with **1** in water using aq TBHP (70%) as the oxygen source resulted in the formation of a mixture of acid **2a** and *p*-methoxy benzonitrile **2b** in 74%, and 20%, respectively, during 36 h (entry 8, Table 2). However, the same reaction under reflux condition furnished a mixture of products **2a** and **2b** in 83% and 12% during a short period (6 h, entry 9, Table 2). It is noteworthy to point out that the reaction of azide **2** with stoichiometric amount of **1** in the absence of oxygen source (in argon atmosphere) did not furnish any product and the starting material was recovered unchanged.[37]

With these information, we continued the investigation on oxidation reaction with a variety of organic azides using V_2O_5 (**1**, 5 mol %) and TBHP (5 equiv) system in aqueous medium. As seen in

Table 2
Oxidation of *p*-methoxybenzyl azide (optimization of oxygen source)



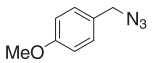
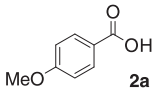
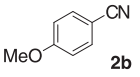
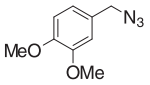
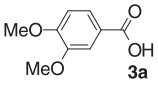
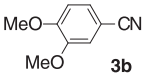
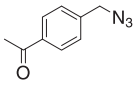
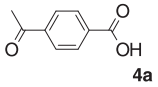
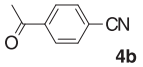
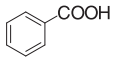
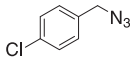
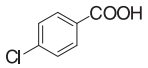
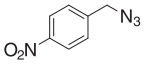
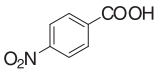
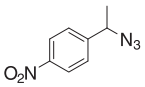
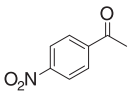
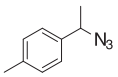
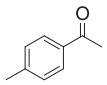
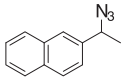
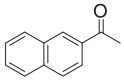
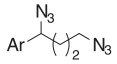
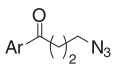
Entry	Oxygen source	Solvent	Temp (°C)	Time (h)	Yield[a] (%)
1	O_2	H_2O	rt	24	NR[b]
2	O_2	H_2O	100	24	NR[b]
3	O_2	Toluene	100	34	NR[b]
4	O_2	EtOAc	rt	24	NR[b]
5	NaOCl(4%)[c]	H_2O	100	24	NR[b]
6	$NaBO_3 \cdot H_2O$[d]	H_2O	100	24	NR[b]
7	aq H_2O_2[e]	H_2O	100	36	NR[b]
8	aq TBHP[f]	H_2O	rt	36	74 (**2a**)
					20 (**2b**)
9	aq TBHP[f]	H_2O	100	6	83 (**2a**)
					12 (**2b**)

[a] Isolated yields.
[b] No reaction.
[c] Solution (4% aq), 2 equiv.
[d] 1.2 quiv.
[e] Solution (50% aq), 5 equiv.
[f] Solution in water (70%), 5 equiv.

Table 3, methoxy substituted benzylic azides such as *p*-methoxybenzyl azide (**2**), and 3,4-dimethoxybenzyl azide (**3**) under the optimized condition produced the corresponding acids **2a** and **3a** as major products along with the corresponding nitriles **2b** and **3b** in minor quantities (entries 1 and 2, Table 3). Similarly, *p*-acetylbenzyl azide, (**4**) with V_2O_5 and TBHP furnished the corresponding acids **4a** as the major product (80%) along with the corresponding nitrile **4b** in minor amount (8%, entry 3, Table 3). In these reactions, our attempts to obtain either acid or nitrile exclusively were unsuccessful.

To test the generality of the oxidation method, a number of azides were subjected to the oxidation catalyzed by **1** (Table 3). Thus, benzyl azide (**5**), *p*-chlorobenzyl azide (**6**), and *p*-nitrobenzyl azide (**7**) afforded the corresponding acids **5a**, **6a**, and **7a** in excellent yields (88, 99, and 90%, respectively, entries 4–6, Table 3). The successful oxidation of azide **7**, which carries electron withdrawing substituent on the benzene ring indicate that the electron withdrawing substituent have no effect on the reaction except that the time taken is longer. Additionally, in these examples of oxidation of **5**, **6**, and **7**, neither aldehyde nor nitrile was observed as the by-products and the corresponding acids were formed exclusively. Further investigation revealed that the oxidation of benzylic azide is general and secondary azides are also readily susceptible for the oxidation to produce the corresponding ketones (Table 3, entries 7–12). Hence, secondary benzylic azides, such as (1-azidoethyl) benzene (**8**), (1-azidoethyl)-4-nitrobenzene (**9**), 1-(1-azidoethyl)-4-methylbenzene (**10**), 2-(1-azidoethyl)naphthalene (**11**), (azidomethylene)dibenzene (**12**), and 4,4′-(azidomethylene)bis(fluorobenzene) (**13**) reacted with **1** to produce corresponding ketones **8a**, **9a**, **10a**, **11a**, **12a**, and **13a**, respectively, in excellent yields (entries 7–12, Table 3). Although benzylic azides underwent a smooth oxidation under the optimized conditions, less active aliphatic azide, such as octyl azide (**14**) failed to undergo oxidation (entry 13, Table 3). As anticipated, phenyl azide (**15**) under the similar reaction condition failed to undergo oxidation and the starting material was recovered unchanged (entry 14, Table 3). By taking advantage of the inertness of inactive primary azide for the oxidation, diazide 1-(4-*tert*-butylphenyl)-1,4-diazidobutane (**16**), was subjected to oxidation. As expected, the oxidation was selective and furnished the corresponding ω-azidoketone **16a** in moderate yield, in which the benzylic azide was oxidized, whereas the terminal primary azido group was intact during the reaction conditions (64%, entry 15, Table 3).[38]

Table 3
Oxidation of primary and secondary benzylic azides by V_2O_5(**1**) and TBHP

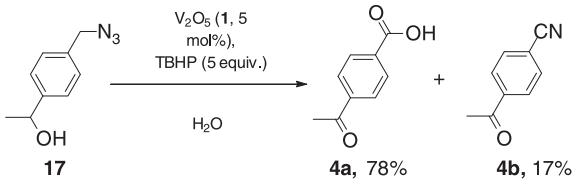
Entry	Substrate		Time (h)	Products		Yields[a] (%)
1		**2**	6	 **2a**	 **2b**	83 (**2a**)+12 (**2b**)
2		**3**	6	 **3a**	 **3b**	83 (**3a**)+13 (**3b**)
3		**4**	6	 **4a**	 **4b**	80 (**4a**)+8 (**4b**)
4		**5**	6		**5a**	88
5		**6**	6		**6a**	99
6		**7**	30		**7a**	90
7		**8**	6		**8a**	93
8		**9**	7		**9a**	97
9		**10**	6		**10a**	63
10		**11**	7		**11a**	99
11		**12**	6		**12a**	99
12	 *Ar* = *p*-Fluorophenyl	**13**	6		**13a**	99
13	*n*-Octyl azide	**14**	24	—		NR[b]
14		**15**	24	—		NR[b]
15	 *Ar* = 4-*t*-*butyl*phenyl	**16**	6		**16a**	64

[a] Isolated yields.
[b] No reaction.

2.2. Oxidation of benzylic alcohols

The present scenario of oxidizing primary and secondary benzylic azides prompted us to investigate the oxidation of alcohols in water medium. Therefore, to find out whether there is any selectivity in the oxidation of benzylic azide in the presence of alcohols, we set a probe with 1-(4-(azidomethyl)phenyl)ethanol (**17**), which contains both azide and alcohol functionality. As seen from Scheme 1, azido alcohol **17** underwent a smooth oxidation with **1** and TBHP at reflux condition to furnish a mixture of 4-acetylbenzoic acid (**4a**), as the major product (78%) along with 4-acetylbenzonitrile (**4b**) in a minor amount (17%) indicating the susceptibility of alcohols for oxidation under the present condition.

A quick survey of literature indicated that V_2O_5 is employed in several oxidations.[9a,17,39] Among them the oxidation of alcohols by V_2O_5 by Punniyamurthy and Velusamy[17] attracted our attention. In

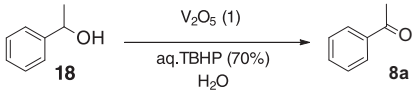


Scheme 1. Oxidation of 1-(4-(azidomethyl)phenyl)ethanol (**17**).

this paper V_2O_5 catalyzed oxidation of alcohols in the presence oxygen using toluene as solvent is described. Additionally, these oxidations require additive, such as K_2CO_3, otherwise the oxidations would lead to the formation of esters through hemiacetals. However, the difference between the present study and the earlier study[17] on the utility of V_2O_5 is as follows: (i) TBHP is employed as the oxidant, (ii) the reaction does not form the corresponding esters, or hemiacetals and, (iii) most importantly, the reaction is performed in water. Apart from this, oxidation of primary alcohols furnished the corresponding acids exclusively in good yields, and aldehyde was not observed in the reaction mixture. The observation that there is no ester formation in the reaction indicates that the reaction is not going through the hemiacetal intermediate under standard reaction condition.[40] Besides this, the acid formed in the reaction does not react further with the alcohol, which is available as the starting material, to form the corresponding ester under the standard reaction condition. In addition, conversion of alcohols to acid directly in one step has advantages when acid is required, which avoids additional step of oxidizing aldehydes to acids.[41] As most of the oxidations catalyzed by V_2O_5 furnish aldehydes, we contemplated that oxidation of alcohols to acids is important, which is an advantage of the present method. Although, there are several methods available for the conversion of alcohols to acids, we believe that the simplicity of the present method is more attractive. Therefore, we thought that there is sufficient scope to pursue the reaction and continued our investigation.

Therefore, we persuaded the oxidation of alcohols, and optimization results are tabulated in Table 4. Hence, we subjected α-methylbenzyl alcohol (**18**) for oxidation using V_2O_5 (**1**) and aq TBHP system under a variety of reaction conditions. Utility of V_2O_5 (**1**) in 0.1 mol % and TBHP in 3 equiv at 100 °C furnished the corresponding ketone **8a** in 65% yield (28 h, entry 1, Table 4). However, increasing the amount of TBHP to 5 equiv resulted in the formation of corresponding ketone **8a** in almost quantitative yield (24h, entry 2, Table 4). Increasing the catalyst loading to 1 mol % and using 4 equiv of TBHP at reflux temperature resulted in the formation of ketone **8a** in 95% in short duration (12 h, entry 3, Table 4). Further, increasing the catalyst loading to 3 mol % or 10 mol % has resulted in marginal improvement of the yields (entries 4–5, Table 4). Although oxidation carried out at room temperature with decreased catalyst loading (1 mol % or 5 mol %) produced corresponding ketone **8a** in quantitative yields, it required longer time to complete the oxidation (entries 6 and 7, Table 4). On the other hand, using stoichiometric amount of **1** in the absence of oxygen source did not afford ketone, but the starting material was isolated unchanged (entry 8, Table 4). Ultimately, it was found that 5 mol % of **1** and 4 equiv of aq TBHP under reflux conditions (entry 9, Table 4) is a suitable condition for the oxidation of α-methylbenzyl alcohol (**18**) to corresponding ketone **8a** in quantitative yield (entry 9, Table 4). In a typical experiment, alcohol **18** (1 mmol), **1** (5 mol %) and aq TBHP (4 equiv) in water (1 mL) were heated at reflux till the completion of the reaction and aqueous work up gave the corresponding carbonyl compound.

Table 4
Optimization of oxidation of alcohols

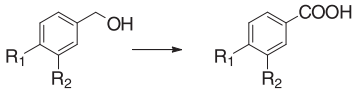


Entry	Catalyst (**1**, mol %)	aq TBHP (equiv)	Temp (°C)	Time (h)	Yield[a] (%)
1	0.1	3	100	28	65
2	0.1	5	100	24	98
3	1	4	100	12	95
4	3	4	100	10	100
5	10	5	100	6	100
6	1	5	rt	28	100
7	5	5	rt	24	100
8	100	—	100	24	NR[b]
9	5	4	100	8	100

[a] Isolated yields.
[b] No reaction.

As seen in Table 5, a variety of primary benzylic alcohols underwent a smooth oxidation under the optimized reaction condition. Benzyl alcohol (**19**), and benzylic alcohols that contain electron donating substituent, such as *p*-methoxybenzyl alcohol (**20**), 3,4-dimethoxybenzyl alcohol (**21**), and *p*-methylbenzyl alcohol (**22**) furnished the corresponding acids **5a**, **2a**, **3a**, and **22a**, respectively, in excellent yields (entries 1–4, Table 5). 4-(Allyloxy)-3-(methoxyphenyl)methanol (**23**) furnished the corresponding acid **23a** in excellent yield (entry 5, Table 5). Interestingly, the allylic functional group was intact during the reaction condition.

Table 5
Oxidation of primary alcohols

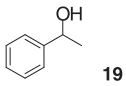
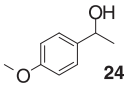
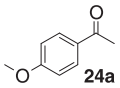
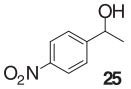
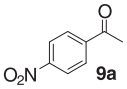
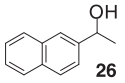
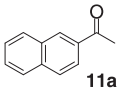
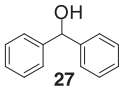
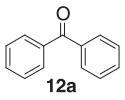
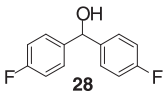
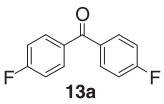
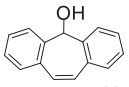
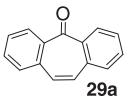
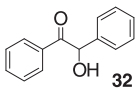
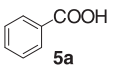
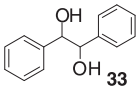
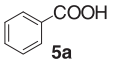
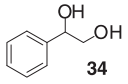
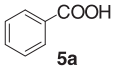


Entry	Substrate		Time (h)	Product	Yield[a] (%)
1	R_1=H R_2=H	**19**	8	**5a**	95
2	R_1=OMe R_2=H	**20**	8	**2a**	99
3	R_1=OMe R_2=OMe	**21**	8	**3a**	98
4	R_1=Me R_2=H	**22**	9	**22a**	74
5	R_1=*O*-allyl R_2=O–Me	**23**	8	**23a**	97

[a] Isolated yields.

This methodology was successfully applied for the oxidation of a variety of secondary alcohols, and corresponding ketones were isolated in excellent yield. As can be seen in Table 6, α-methylbenzyl alcohol (**19**), 1-(*p*-methoxyphenyl)-1-methylethanol (**24**), (*p*-nitrophenyl)-1-methylethanol (**25**), and 1-(naphthalen-2-yl)ethanol (**26**) furnished corresponding ketones **8a**, **24a**, **9a**, and **11a**, respectively, in good yields (entries 1–4, Table 6). Similarly, diphenylmethanol (**27**), bis(4-fluorophenyl)methanol (**28**), and 5*H*-dibenzo[*a*,*d*][7]annulen-5-ol (**29**) underwent a smooth oxidation to afford the corresponding ketones **12a**, **13a**, and **29a** in excellent yields (entries 5–7, Table 6). Less active secondary alcohols, such as 2-methyl-1-octonal (**30**) and cyclohexanol (**31**) furnished the corresponding ketones **30a** and **31a** in good yields (entries 8–9, Table 6). It is important to recall that the aliphatic azides were inert under the reaction condition whereas, the corresponding secondary alcohols were oxidized successfully. Our attempt to synthesize 1,2-diketones from β-hydroxy ketones did not furnish the corresponding 1,2-diketone, but resulted in the cleavage of C–C bond (entries 10–12, Table 6). Hence, 2-hydroxy-1,2-diphenylethanone (**32**) furnished benzoic acid (**5a**). As 1,2-diketones and 1,2 diols are known to react with peroxides to furnish corresponding acid,[42] we believe that the diketone, which is formed under the reaction is

Table 6
Oxidation of secondary alcohols

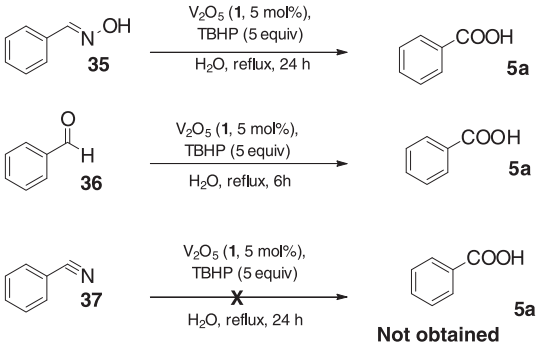
Entry	Substrate	Time (h)	Product	Yield[a] (%)
1	 **19**	8	 **8a**	76
2	 **24**	8	 **24a**	84
3	 **25**	23	 **9a**	83
4	 **26**	24	 **11a**	97
5	 **27**	8	 **12a**	99
6	 **28**	24	 **13a**	94
7	 **29**	20	 **29a**	65
8	 **30**	8	 **30a**	95[b,c], NR[d,e]
9	 **31**	8	 **31a**	65[b,c], NR[d,e]
10	 **32**	6	 **5a**	82
11	 **33**	6	 **5a**	82
12	 **34**	6	 **5a**	85

[a] Isolated yields.
[b] GC yields.
[c] Neat reaction.
[d] Reaction in water.
[e] NO reaction.

undergoing cleavage to generate benzoic acid. Similarly, 1,2-diols, such as 1,2-diphenylethane-1,2-diol (**33**), 1-phenylethane-1,2-diol (**34**) underwent the similar reaction to produce benzoic acid (entries 11 and 12, Table 6).

2.3. Mechanistic studies

We believe that the reaction of V_2O_5 (**1**) with TBHP would generate an intermediate, which may be responsible for the present oxidation. Oxidation of azide **2** with V_2O_5 (**1**, 5 mol %) and TBHP (5 equiv) in the presence of radical scavenger such as BHT (butylated hydroxytoluene or 2,6-bis(1,1-dimethylethyl)-4-methylphenol) failed to give the corresponding acid **2a** and the starting material recovered unchanged. This observation indicates that the oxidation is going through radical pathway. Additionally, oxidation of azide **2** with stoichiometric amount of V_2O_5 (**1**), in the absence of TBHP did not furnish the expected product but the starting material was recovered unchanged. This reaction indicates that the species generated by the reaction of **1** with TBHP in the presence of azide may be held responsible for the catalytic oxidation. However, our attempts to understand the mechanism by recording ^{51}V NMR of different intermediates did not yield any conclusive results. Therefore, we performed few control experiments (Scheme 2) as presented in the following section. Benzaldoxime (**35**) under the optimized reaction condition afforded the corresponding acid **5a** in quantitative yield, whereas benzaldehyde (**36**) was completely oxidized to the corresponding acid **5a** in quantitative yield. However, benzonitrile (**37**) did not furnish the corresponding acid **5a** and the starting material was intact under the reaction condition. These experiments suggest that, probably nitrile may not be the intermediate but the reaction may go through an oxime intermediacy, which is oxidized to aldehyde and finally to the corresponding acid. As far as the oxidations of alcohol are concerned, we believe that the reaction goes through the redox pathway. Further, studies are in progress to get light on mechanism of oxidation of azides as well as alcohols.



Scheme 2. Control experiments.

3. Conclusion

In summary, we have carried out an elaborated investigation on the oxidation reaction of azides and alcohols using catalytic amount of vanadium pentoxide (5 mol %) and TBHP in aqueous medium. The outcome of the present research is that, benzylic azides are conveniently oxidized to the corresponding acids and ketones. Furthermore, primary and secondary alcohols are also oxidized to the corresponding acids and ketones, respectively. Unlike known methods, the present method does not form the corresponding ester or hemiacetal. Our attempts to obtain nitrile exclusively in the above reaction were not successful. The preliminary studies conducted on the mechanistic study indicate that the oxime might be the intermediate in the oxidation of azides, whereas the oxidation

of alcohol may follow the typical redox reaction. Further studies to throw more light on the mechanism and kinetic resolution studies of secondary alcohols and azides are underway in our laboratory.

4. Experimental

4.1. General information

All solvents were dried and distilled according to standard methods before use. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. Tetramethylsilane (TMS; δ=0.00 ppm) and residual non-deuterated DMSO signal (δ=2.49 ppm) served as internal standards for ^{1}H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$: δ=77.00 ppm; DMSO: δ=39.50 ppm) was used as internal standards for ^{13}C NMR. NMR spectra were recorded on a BRUKER-AV400 and JEOL LA-300, spectrometer in $CDCl_3$ and DMSO-d_6. Tetramethylsilane (TMS; δ=0.00 ppm) and residual non-deuterated DMSO signal (δ=2.49 ppm) served as internal standards for 1H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$: δ=77.00 ppm; DMSO: δ=39.50 ppm) was used as internal standards for ^{13}C NMR. IR spectra were measured using a JASCO FT/IR-410 spectrometer, and Perkin–Elmer FT/IR Spectrum BX, GX. Mass spectra were measured with Micromass Q-Tof (ESI-HRMS), and GC–MS shimadzu. Column chromatography was conducted on Silica gel 230–400 mesh (Merck) and preparative thin-layer chromatography was carried out using SILICA GEL GF-254. All melting points were measured on a 'Buchi Melting Point B-540' apparatus and are uncorrected. Elemental analysis was carried out at the Department of Organic Chemistry, Indian Institute of Science, Bangalore, India by using Thermo Finnigan Flash 1112 series analyser.

4.2. Typical experimental procedure for oxidation of azides to acid

To a well-stirred suspension of azide (1 mmol) and V_2O_5 (**1**, 0.05 mmol) in water (1 mL) was added aq TBHP (70%, 5 mmol). The reaction mixture was heated at reflux until the completion of the reaction (monitored by TLC). The reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to furnish crude acid, which was purified on a silica gel column (EtOAc/hexane). In case of problem in isolating acids, the solvent was evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (EtOAc/hexane).

4.3. Typical experimental procedure for oxidation of alcohols

To a well-stirred suspension of alcohol (1 mmol) and V_2O_5 (0.05 mmol) in water (1 mL) was added aq TBHP (70%, 4 mmol). The reaction mixture was heated at reflux until the completion of the reaction (monitored by TLC). The reaction mixture was extracted with ethyl acetate (3×15 mL). The combined organic layer was dried over Na_2SO_4 and evaporated under vacuum to furnish the crude product, which was purified on a silica gel column using EtOAc and hexane as the solvent mixture. In case of problem in isolating the acid, the solvent was evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (EtOAc/hexane).

4.4. Oxidation of 2: oxidation of 3 furnished mixture 4-methoxybenzoic acid (2a) in 83% and 4-methoxybenzonitrile (2b) in 14%

*4.4.1. 4-Methoxybenzoicacid (**2a**)*[43]. Colorless solid; Yield: 83%; mp: 181–183 °C (lit.[43] 180–182 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 3428, 1682; ^{1}H NMR (400 MHz, DMSO): δ 7.87(2H, d, *J* 8.6 Hz), 6.98 (2H, d, *J* 8.6 Hz), 3.78 (3H, s); ^{13}C NMR (100 MHz, DMSO): 167.4, 162.9, 131.5, 123.4, 113.9, 55.6; MS (*m*/*z*)=152(M$^+$).

*4.4.2. 4-Methoxybenzonitrile (**2b**)*[44]. Colorless solid; yield: 14%; mp: 60–61 °C (lit.[44] 61–62 °C); R_f (20% EtOAc/hexane) 0.40; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 5:95 to 10:90); IR (neat, cm^{-1}): 2219; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58(2H, d, *J* 8.7 Hz), 6.95 (2H, d, *J* 8.7 Hz), 3.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 162.7, 133.9, 119.1, 114.6, 103.8, 55.4; MS (*m*/*z*)=133 (M$^+$).

4.5. Oxidation of 3: oxidation of 3 furnished mixture 3, 4-dimethoxybenzoic acid (3a) in 83% and 3,4-dimethoxybenzonitrile (3b) in 13%

*4.5.1. 3,4-Dimethoxybenzoic acid (**3a**)*[43]. Colorless solid; yield: 83%, mp: 176–178 °C (lit.[43] 178–180 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 1681; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (1H, d, *J* 8.4 Hz), 7.60 (1H, s), 6.92 (1H, d, *J* 8.4 Hz), 3.96 (3H, s), 3.95 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 171.9, 153.6, 148.6, 124.5, 121.6, 112.2, 110.2, 56.0, 55.9; MS (*m*/*z*)= 182 (M$^+$).

*4.5.2. 3,4-Dimethoxybenzonitrile (**3b**)*[45]. Colorless solid; yield: 13%, mp: 67–68 °C (lit.[45] 68 °C); R_f (10% EtOAc/hexane) 0.40; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 5:95 to 10:90); IR (neat, cm^{-1}): 2225; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (1H, d, *J* 8.3 Hz), 7.08 (1H, s), 6.91 (1H, d, *J* 8.3 Hz), 3.93 (3H, s), 3.90 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 152.7, 149.0, 126.3, 119.1, 113.8, 111.1, 103.7, 56.04, 56.00; MS (*m*/*z*)=163 (M$^+$).

4.6. Oxidation of 4: oxidation of 4 furnished the mixture of 4-acetylbenzoic acid (4a) in 82% and 4-acetylbenzonitrile (4b) in 17%

*4.6.1. 4-Acetylbenzoicacid (**4a**)*[46]. White solid; yield: 82%; mp: 211–212 °C (lit.[46] 213–215 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 1688, 1682; ^{1}H NMR (400 MHz, Acetone): δ 8.14(2H, d, *J* 8.4 Hz), 8.09 (2H, d, *J* 8.4 Hz), 2.64 (3H, s); ^{13}C NMR (100 MHz, acetone): 197.6, 166.8, 141.3, 135.0, 130.6, 129.0, 26.9; MS (*m*/*z*)=164(M$^+$).

*4.6.2. 4-Acetylbenzonitrile (**4b**)*[47]. White solid; yield: 17%; mp: 60–62 °C (lit.[47] 58–60 °C); R_f (20% EtOAc/hexane) 0.40; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 5:95 to 15:85); IR (KBr, cm^{-1}): 2229, 1688; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (2H, d, *J* 8.2 Hz), 7.78 (2H, d, *J* 8.2 Hz), 2.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 196.4, 139.8, 132.4, 128.6, 117.8, 116.3, 26.7; MS (*m*/*z*)=(M$^+$).

*4.6.3. Benzoic acid (**5a**)*[46]. Colorless solid; yield: 88%, mp: 123–125 °C (lit.[43] 124–126 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 3430,1673; ^{1}H NMR (400 MHz, DMSO): δ 7.94 (2H, d, *J* 7.6 Hz), 7.47–7.50 (1H, m), 7.38–7.42 (2H, m); ^{13}C NMR (100 MHz, DMSO): 169.0, 134.2, 131.6, 129.3, 128.2; MS (*m*/*z*)=122(M$^+$).

*4.6.4. 4-Chlorobenzoic acid (**6a**)*[46]. White solid; yield: 99%, mp: 236–237 °C (lit.[46] 236–238 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on

silica gel (EtOAc/hexane) 20:80 to 30:70; IR (KBr, cm^{-1}): 1683; ^1H NMR (400 MHz, DMSO): δ 7.92 (2H, d, *J* 8.4 Hz), 7.55 (2H, d, *J* 8.4 Hz); ^{13}C NMR (100 MHz, DMSO): 166.4, 137.8, 131.1, 129.6, 128.7; MS (*m*/*z*)=156 (M^+).

*4.6.5. 4-Nitrobenzoic acid (**7a**)*[46]. Light yellow solid; yield: 90%, mp: 242–244 °C (lit.[46] 240–242 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane) 20:80 to 30:70; IR (KBr, cm^{-1}): 1699; ^1H NMR (400 MHz, DMSO): δ 8.31 (2H, d, *J* 8.8 Hz), 8.15 (2H, d, *J* 8.8 Hz); ^{13}C NMR (100 MHz, DMSO): 165.8, 150.0, 136.3, 130.7, 123.7; MS (*m*/*z*)=167 (M^+).

*4.6.6. Acetophenone (**8a**)*[44,48]. Colorless liquid; yield: 93%, R_f (20% EtOAc/hexane) 0.50; Prepared as shown in general experimental procedure. IR (neat, cm^{-1}): 1691; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (1H, d, *J* 8 Hz), 7.50–7.54 (1H, m), 7.40–7.44 (2H, m), 2.56 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 198.1, 136.9, 132.9, 128.4, 128.1, 26.4; MS (*m*/*z*)=120 (M^+).

*4.6.7. 4-Nitroacetophenone (**9a**)*[44,48]. Yellowish white solid; yield: 97%, mp: 78–79 °C (lit.[44,48] 80–81 °C); R_f (20% EtOAc/hexane) 0.50; prepared as shown in general experimental procedure. IR (KBr, cm^{-1}): 1694; ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (2H, d, *J* 8.4 Hz), 8.12 (2H, d, *J* 8.4 Hz), 2.70 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 196.2, 150.2, 141.2, 129.2, 123.7, 26.9; MS (*m*/*z*)=165 (M^+).

*4.6.8. 4-Methylacetophenone (**10a**)*[49]. Colorless liquid; yield: 63%, R_f (20% EtOAc/hexane) 0.65; prepared as shown in general experimental procedure. IR (neat, cm^{-1}): 1682; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (2H, d, *J* 8 Hz), 7.25 (2H, d, *J* 8 Hz), 2.57 (3H, s), 2.40 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 197.8, 143.8, 134.6, 129.1, 128.3, 26.4, 21.5; MS (*m*/*z*)=134 (M^+).

*4.6.9. 1-(Naphthalen-2-yl)ethanone (**11a**)*[49]. White solid; yield: 99%, mp: 53–55 °C (lit.[49] 53–54 °C); R_f (20% EtOAc/hexane) 0.60; prepared as shown in general experimental procedure. IR (neat, cm^{-1}): 1678; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (1H, s), 8.02 (1H, dd, *J* 1.7, 8.6 Hz), 7.95 (1H, d, *J* 8 Hz), 7.85–7.88 (2H, m), 7.52–7.60 (2H, m), 2.71 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 198.0, 135.5, 134.4, 132.4, 130.1, 129.4, 128.4, 128.3, 127.7, 126.7, 123.8, 26.6; MS (*m*/*z*)=170 (M^+).

*4.6.10. Benzophenone (**12a**)*[44,48]. White solid; yield: 99%, mp: 50–51 °C (lit.[44,48] 48–50 °C); R_f (20% EtOAc/hexane) 0.75; prepared as shown in general experimental procedure. IR (KBr, cm^{-1}): 1659; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (4H, d, *J* 8.4 Hz), 7.56–7.60 (2H, m), 7.44–7.48 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 196.6, 137.4, 132.3, 129.9, 128.1; MS (*m*/*z*)=182 (M^+).

*4.6.11. 4,4′-difluorobenzophenone (**13a**)*[50]. White solid; yield: 99%, mp: 101–103 °C (lit.[50] 103–105 °C); R_f (5% EtOAc/hexane) 0.60; prepared as shown in general experimental procedure. IR (KBr, cm^{-1}): 1649; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79–7.83 (4H, m), 7.14–7.20 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 193.8, 166.6, 164.1, 133.69, 133.66, 132.5, 132.4, 115.6, 115.4; MS (*m*/*z*)=218 (M^+). HRESI-MS (*m*/*z*) Calculated for $C_{13}H_8F_2O$ (M+H): 219.0621, found (M+H): 219.0612.

*4.6.12. 1-(4-tert-Butylphenyl)-4-azidobutan-1-one (**16a**).* Pale pink liquid; yield: 64%, R_f (10% EtOAc/hexane) 0.60; prepared as shown in general experimental procedure. IR (neat, cm^{-1}): 2098, 1683; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (2H, d, *J* 8.6 Hz), 7.48 (2H, d, *J* 8.6 Hz), 3.40 (2H, t, *J* 6.6 Hz), 3.06 (2H, t, *J* 7.0 Hz), 2.02–2.05 (2H, m), 1.34 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 198.5, 156.9, 134.1, 127.9, 125.5, 50.8, 35.09, 35.0, 31.0, 23.3; HRESI-MS (*m*/*z*): calculated for $C_{14}H_{19}N_3O$ (M+Na): 268.1426, found (M+Na): 268.1421.

*4.6.13. 4-Methylbenzoicacid (**22a**)*[51]. Colorless solid; yield: 4%; *mp*: 174–177 °C (lit.[46] 175–178 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 1681; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00(2H, d, *J* 7.8 Hz), 7.26 (2H, d, *J* 7.8 Hz), 2.42(3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 172.4, 144.5, 130.2, 129.1, 126.6, 21.7; MS (*m*/*z*)=136(M^+).

*4.6.14. 4-Allyloxy-3-methoxybenzoic acid (**23a**)*[52]. White solid; yield: 97%, mp: 176–178 °C (lit.[52] 175–176 °C); R_f (20% EtOAc/hexane) 0.05; prepared as shown in general experimental procedure. Purified on silica gel (EtOAc/hexane 20:80 to 30:70); IR (KBr, cm^{-1}): 3446, 1676; ^1H NMR (400 MHz, MeOH): δ 7.57 (2H, m), 6.91 (1H, d, *J*=10.8 Hz), 5.40 (1H, dd, J_1 1.5, 17.2 Hz), 5.25 (1H, dd, *J* 1.3, 10.4 Hz), 4.61 (2H, d, *J* 5.2 Hz), 3.87 (3H, s); ^{13}C NMR (100 MHz, MeOH): 173.8, 151.8, 149.9, 134.6, 124.0, 117.9, 115.3, 114.1, 113.4, 70.7, 56.3; MS (*m*/*z*)=208(M^+).

*4.6.15. 1-(4-Methoxyphenyl)ethanone (**24a**)*[44,48]. Colorless liquid; yield: 84%, R_f (20% EtOAc/hexane) 0.50; prepared as shown in general experimental procedure. IR (neat, cm^{-1}): 1676; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (2H, d, *J* 8.4 Hz), 6.92 (2H, d, *J* 8.4 Hz), 3.85 (3H, s), 2.55 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 196.8, 163.3, 130.5, 130.1, 113.5, 55.3, 26.2; HRESI-MS (*m*/*z*): Calculated for $C_9H_{10}O_2$ (M+H): 151.0759, found (M+H): 151.0759.

*4.6.16. 5H-Dibenzo(a,d)(7)annulen-5-one (**29**)*[53]. White solid; yield: 65%, mp: 85–86 °C (lit.[53] 87–88 °C); R_f (5% EtOAc/hexane) 0.60; prepared as shown in general experimental procedure. IR (KBr, cm^{-1}): 1645, 1590; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (2H, d, *J* 8.3 Hz), 7.60–7.66 (2H, m), 7.52–7.55 (4H, m), 7.05 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 193.0, 138.6, 134.8, 134.1, 131.9, 131.6, 130.7, 130.1, 128.8; HRESI-MS (*m*/*z*): calculated for $C_9H_{10}O_2$ (M+H): 207.0810, found (M+H): 207.0821.

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Supplementary data

^1H and ^{13}C NMR spectra are available for all products. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.080.

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