

Vanadium-Catalyzed Selective Oxidation of Alcohols to Aldehydes and Ketones with *tert*-Butyl Hydroperoxide

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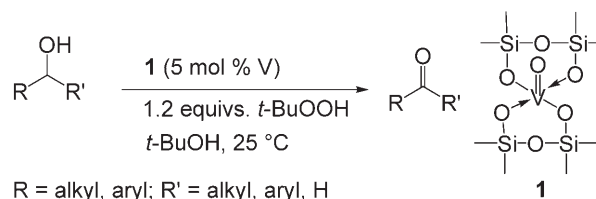


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Abstract: The oxidation of alcohols to aldehydes and ketones has been described using silica-supported vanadium(IV) oxide (V/SiO₂, **1**) in the presence of *tert*-butyl hydroperoxide in *tert*-butyl alcohol at ambient temperature with quantitative yields. The procedure is simple, efficient and environmentally benign.

Keywords: alcohols; *tert*-butyl hydroperoxide; catalyst; oxidation; vanadium

The oxidation of alcohols to aldehydes and ketones is one of the fundamental processes in organic synthesis.^[1,2] The traditional methods for this purpose usually employ stoichiometric quantities of inorganic reagents such as chromate and permanganate, which often generate significant amount of inorganic salt-containing effluent along with the target molecules.^[3] Removal of traces of these effluents from the reaction mixture is often difficult and demands laborious work-up procedures. To circumvent this problem, much attention has been recently focused on the design and development of catalytic systems, especially without reducing agents in ecologically benign conditions to reduce the environmental impact of the process (E factor).^[4–13] During the course of our investigation on the oxidation of organic compounds,^[13] we found that the silica-supported vanadium(IV) oxide **1** catalyzed efficiently the oxidation of heteroatoms with 30 % H₂O₂ in high yields.^[14] Since the catalyst **1** is readily accessible, cheap and provides simplified product isolation, we wanted to further explore its application to other reactions. In this contribution, we report the oxidation of alcohols to aldehydes and ketones in the presence of *tert*-butyl hydroperoxide (*t*-BuOOH) in *tert*-butyl alcohol (*t*-BuOH) at ambient temperature (Scheme 1). It is a clean technological process and no additive is involved. Since the reac-



Scheme 1.

tions usually take place with 100 % conversion, after filtering the catalyst **1**, the filtrate could be evaporated to provide the aldehydes or ketones as the only products.

The oxidation of *p*-anisyl alcohol was first studied as a standard substrate using **1** in the presence of *t*-BuOOH at ambient temperature (Table 1). We were pleased to find that the reaction occurred to afford *p*-anisaldehyde in quantitative yield when it was allowed to stir with 15 mg of **1** (5 mol % V) and 1.2 equivs. of *t*-BuOOH (5 M in decane) for 3 h in *t*-

Table 1. Oxidation of anisyl alcohol.^[a]

Entry	Catalyst	Oxidant	pH	Product(s) [%] ^[b]	
				RCHO	RCOOH
1	1	<i>t</i> -BuOOH	5.23	>99	0
2 ^[c]	VO(acac) ₂	<i>t</i> -BuOOH	3.83	38	21
3	1	30% H ₂ O ₂	2.63	trace	-
4	1	50% H ₂ O ₂	2.03	14	6
5	1	UHP	-	-	-

^[a] Substrate (1 mmol), ROOH (1.2 mmol) and catalyst **1** (15 mg, 5 mol % V) were stirred in *t*-BuOH (1 mL) at ambient temperature for 3 h.

^[b] R = *p*-MeOC₆H₄-.

^[c] *t*-BuOOH was consumed in 1 h.

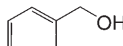
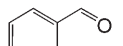
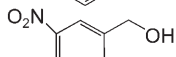
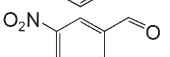
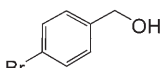
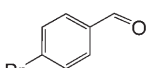
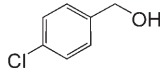
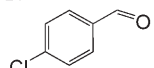
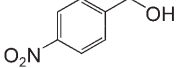
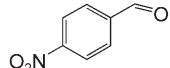
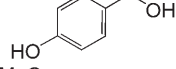
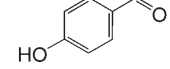
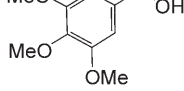
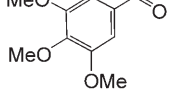
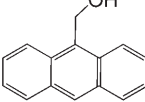
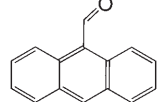
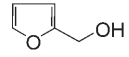
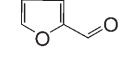
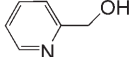
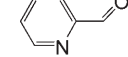
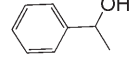
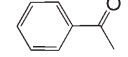
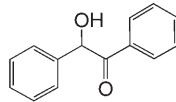
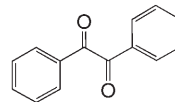
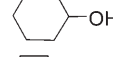
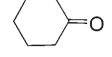
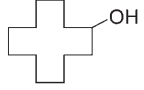
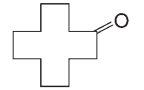
BuOH. Hydrogen peroxides [30–50 % H_2O_2 and urea hydrogen peroxide (UHP)] were also investigated as terminal oxidants, but they are less effective providing either no reaction or a mixture of aldehyde and carboxylic acid in moderate yield (entries 3–5).^[15] Also, the reaction with $\text{VO}(\text{acac})_2$ was found to be efficient, but less selective giving a mixture of *p*-anisaldehyde and *p*-anisic acid in 38 % and 21 % yields, respectively.

To study the scope of the procedure, the oxidation of other alcohols was next studied (Table 2). Benzyl alcohols were oxidized to give the corresponding aldehydes with 100 % conversion (entries 1–7). The substrates having electron-donating and -withdrawing substituents in the aromatic ring were compatible with this protocol. 9-Anthracenemethanol, 2-furanmethanol and 2-pyridinemethanol were transformed to the respective aldehydes in high yields (entries 8–10). It is noteworthy that the reactions stopped at the aldehyde stage without overoxidation to the carboxylic acid. Secondary alcohols, e.g., 1-phenylethanol and benzoin, could be converted to the respective ketones in >99 % yields (entries 11 and 12). Aliphatic alcohols were less reactive in comparison to aromatic alcohols. The oxidations of cyclohexanol and cyclododecanol were studied (entries 13 and 14). They required longer reaction times and were effective in the presence of 10 mol % of **1** and 2 equivs. of *t*-BuOOH to afford the corresponding ketones. Similarly, allylic alcohols, such as cinnamyl alcohol and geraniol, underwent oxidation to give a mixture of the corresponding epoxy alcohols and aldehydes.^[16]

The difference in the reactivity of **1** with *t*-BuOOH and H_2O_2 might be due to the pH and nature of the peroxide involved in the reaction process (Table 1).^[17] Since the systems of 50 % H_2O_2 /**1** and *t*-BuOOH/ $\text{VO}(\text{acac})_2$ are found to be more acidic (pH 2.03–3.83) than *t*-BuOOH/**1** (pH 5.23), the former may lead to the formation of a hydrate which would undergo subsequent oxidation to its carboxylic acid. Furthermore, peroxo complexes formed in these reactions should also be different since their formation depends on the pH of the medium.^[17] The reaction of **1** with 50 % H_2O_2 generates brown-colored species while the combination of **1** and *t*-BuOOH produces a yellow complex. Thus, the electrophilic character of the peroxo oxygen atoms might also be different leading to variation in the reactivity toward aldehydes. When these peroxo species are quenched with Na_2SO_3 or consumed during the oxidation processes, the color of the catalyst changes to its initial green color [V(IV)] (Scheme 2).^[18,19] The solid could be then filtered and the filtrate, after evaporation, provides the corresponding carbonyl compounds which usually do not require further purification.

Finally, the oxidation of *p*-anisyl alcohol was studied on a 100-mmol scale. As above, the reaction oc-

Table 2. Vanadium-catalyzed oxidation of alcohols to aldehydes and ketones with *t*-BuOOH.

Entry	Substrate	Time [h]	Product	Yield [%] ^[a,b]
1		3		>99
2		3		>99
3		4		>99
4		4		>99
5		5		>99
6		3		>99
7		5		>99
8		5		>99
9		4		>99
10		5		>99
11		5		>99
12		10		>99
13 ^[c]		25		95
14 ^[c]		25		87

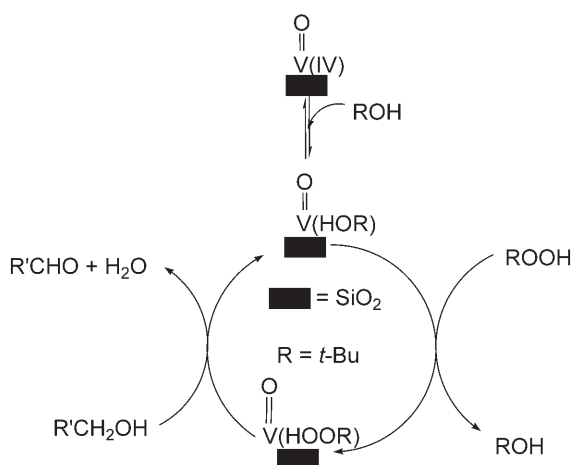
^[a] Substrate (1 mmol), *t*-BuOOH (1.2 mmol, 5 M in decane) and catalyst **1** (15 mg, 5 mol % V) were stirred in *t*-BuOH (1 mL) at ambient temperature.

^[b] Isolated yield.

^[c] Catalyst **1** (10 mol %, 30 mg) and *t*-BuOOH (2 mmol) were used.

curred to afford *p*-anisaldehyde in 95 % yield. This result suggests that the present system could be used for medium-scale syntheses.

In conclusion, the vanadium catalyst **1** has been found to catalyze efficiently the oxidation of alcohols to aldehydes and ketones in the presence of *t*-BuOOH in *t*-BuOH at ambient temperature. It is a



Scheme 2.

clean technological process and no halogenated solvents are involved.

Experimental Section

Typical Procedure for the Oxidation of Alcohols

To a stirred solution of the alcohol (1 mmol) and catalyst V/SiO₂ **1** (5 mol%, 15 mg) in *t*-BuOH (1 mL) at 25°C, *t*-BuOOH (1.2–2 mmol, 5 M solution in decane) was added. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion, the reaction mixture was quenched with Na₂SO₃ (10 mg). The salt was then filtered and the filtrate was evaporated on a rotary evaporator to afford the products.

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- [18] The excess peroxide was removed by stirring with Na₂SO₃ until the catalyst returns to its initial green color.
- [19] These peroxo complexes undergo decomposition during filtration and show no catalytic activity for the oxidation in the absence of *t*-BuOOH.