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A new alkyl peroxovanadium catalyst for selective oxidation of nitriles to α-oxo nitriles: A functional mimic of Cyt-P.450 [1]

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Abstract

Alkyl peroxovanadium complex catalysed functionalisation of methylene of benzyl cyanides to afford peroxo nitriles or aroyl cyanides selectively depending on the molar quantities of oxidant, *tert* butyl hydroperoxide (*t*-BuOOH) used is described for the first time.

Keywords: Alkyl peroxovanadium complex; Catalytic oxidation; Benzyl cyanides; Aroyl cyanides; Peroxo benzyl cyanides

1. Introduction

Activation of C–H bond of saturated hydrocarbons presents one of the most challenging problems in the area of homogeneous catalysis. In nature, biological activation of alkane C–H bond is accomplished by the heme containing monooxygenases, exemplified by the cytochrome P-450 group of enzymes. Model reactions of the cytochrome P-450 have been studied extensively in view of synthetic [1] and biological aspects [2]. Vanadium(V) peroxo complexes which homolytically cleave to give electrophilic reactive V(IV)–OO species, analogous to that of Fe(III)–OO species of cyt-P.450, can be regarded as valuable models for P-450 dependent monooxygenases [3]. With the discovery of bromo peroxidase vanadium(V) containing enzyme, which is isolated primarily from marine algae catalyses the oxidation of halides Br^-, Cl^-, I^- by hydrogen peroxide [4,5]. Later, a functional model, mimicking the enzyme reactivity in the said halogenation reactions, was developed [6]. These works prompted us to develop new peroxovanadium complexes and employed in the diversified organic transformations such as oxidation of cyclic acetal to glycolmonoesters [7], aralkenes to corresponding benzaldehydes [8]. Herein we describe the peroxovanadium complex conceived and developed by us acting as a functional mimic of cyt-P.450 in catalytic functionalisation of nitriles to α-oxo nitriles.

Acyl cyanides are versatile synthetic intermediates and have been utilised in a variety of transformation of CO and CN functions [9]. This class of compounds have substantially

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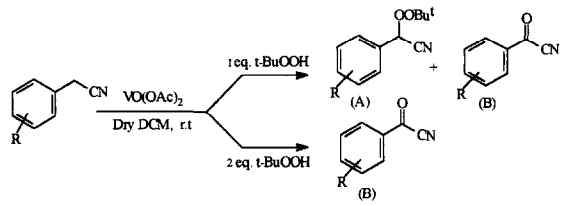
gained importance as building blocks of heterocycles or herbicides. Generally, acyl cyanides have been prepared by the reaction of acid halides with metal cyanides [10] or trimethylsilyl cyanides [11] and the oxidation of cyanohydrins [12,13]. Requirement of stoichiometric amounts of highly toxic and moisture sensitive cyanating reagents render these reactions inconvenient to use in the laboratory. The development of an efficient and alternative to the volatile, toxic cyanating methods for the synthesis of α-oxo benzyl cyanides has been sought for many years. Functionalisation of benzyl cyanides could be considered as a fascinating route to obtain aroyl cyanides or cyanohydrins as an alternative to the cyanation procedures. Our earlier success of functionalisation of phenyl acetic acid esters to corresponding α-keto esters using vanadium pillared clay (V-PILC), a heterogeneous catalyst [14] prompted us to attempt the oxidation of benzyl cyanides with V-PILC and Cr-PILC under the same reaction conditions but were futile and resulted in the formation of benzoic acid. Therefore, we undertook the development of a methodology which can oxygenate the α-methylene of benzyl cyanides to give aroyl cyanides or cyanohydrins with peroxovanadium complex. In the present communication, we report a simple and elegant methodology for the oxidation of benzyl cyanides to either peroxo benzyl cyanides or aroyl cyanides selectively depending upon the use of one or two equivalents *t*-BuOOH of, respectively, using an alkyl peroxovanadium complex, formed in situ from vanadyl acetate for the first time.



Scheme 1.

2. Results and discussion

In this communication, we present the results that demonstrates the synthetic scope of the new peroxovanadium complex developed by us for the oxidation of various benzyl cyanides in conjunction with *t*-BuOOH in dichloromethane at room temperature (Scheme 1).

Table 1 summarises representative results of oxidation of various benzyl cyanides into corresponding peroxides (A) when one equiv. of *t*-BuOOH taken as an oxidant during the reaction. Furthermore, the oxidation of *o*-methoxy benzyl cyanides with one equiv. of *t*-BuOOH under the same reaction conditions gave 2(*tert* butyl dioxy)2(*o*-methoxy phenyl) acetonitrile with excellent selectivity (> 99%) (entry 3). This high selectivity is ascribed to the steric factors which may be preventing the decomposition of peroxides formed in the reaction to aroyl

Table 1
Oxidation of benzyl cyanides to the corresponding α-oxo nitriles using vanadyl acetate

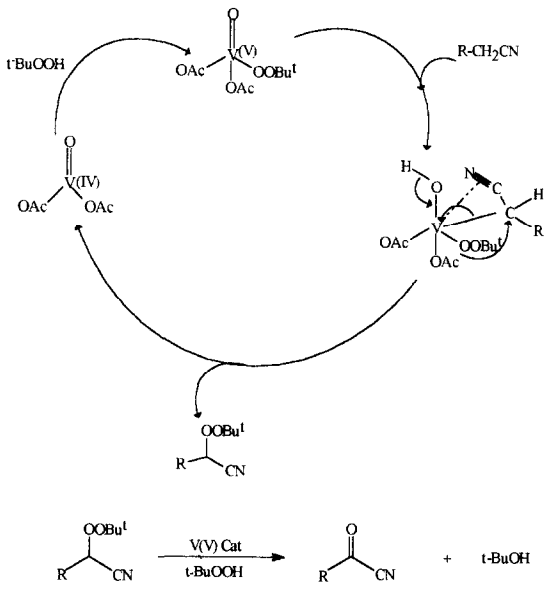
Entry	*R*	1 eq. *t*-BuOOH		2 eq. *t*-BuOOH
		yield[a] (A + B)[b] (%)	selectivity (A:B) (%)	yield[a] (B)[b] (%)
1	H	91	85:15	92
2	*p*-Cl	86	88:12	96
3	*o*-OCH_3	94	99:—	94
4	*p*-NO_2	82	83:17	89
5	*p*-OH	87	86:14	94
6	*p*-CH_3	89	75:25	97
7	*p*-OCH_3	96	92:8	98

[a]Isolated yields.
[b]Products were characterised by ^{1}NMR, mass and IR.

cyanides. A striking feature of the reaction that merits its emphasis is the peroxide formation (A), which on catalytic hydrogenation gives corresponding cyanohydrins. The present method is a simple and superior to the cyanosilylation to prepare cyanohydrins which suffers from serious disadvantages such as siloxy nitrile protective groups inherently unstable to both nucleophiles and aq. media to generate carbonyl derivative [15,16].

The results of the selective oxidation of benzyl cyanides irrespective of the substituent present on the aromatic ring into corresponding aroyl cyanides (B) quantitatively when two equiv. of *t*-BuOOH used as an oxidant are also described in the table. In case of *p*-nitro benzyl cyanides, our procedure is the unquestionable method of choice to obtain *p*-nitrobenzoylcyanides in excellent yield (89%) after 24 h at room temperature (entry 4). By contrast, attempts to prepare this compound in satisfactory yield by previous available cyanation procedures have been reported unsuccessful.

The reaction can be rationalised by assuming Cyt-P.450 type mechanism. A vanadyl acetate reacts with *t*-BuOOH to give alkyl peroxovanadium(V) complex [17,18] which in turn cleaves homolytically to give V–O–O species analogous to that of Fe–O–O species of cyt-P.450, and abstracts a proton from the methylene of benzyl cyanides to give a radical intermediate. Electron transfer followed by nucleophilic attack of *t*-BuOOH complete the catalytic cycle. Further, the excess of *t*-BuOOH oxidises peroxides in the presence of vanadium(V) to aroyl cyanides (Scheme 2).



Scheme 2.

In conclusion, the present simple and catalytic methodology is the unique and unequivocally the method of choice for the synthesis of aroyl cyanides or cyanohydrins by selective functionalisation of readily available benzyl cyanides and could be a practical alternative to the existing highly volatile trimethyl silyl cyanide, other toxic cyanating methods available in the literature.

3. Experimental

The structural assignment of the reaction products were corroborated by spectral analysis ^{1}H NMR spectra were recorded with Varian Gemini (200 MHz) NMR spectrometer, IR spectra recorded using Nicolet DX-5 and Mass spectra with micromass VG 7070H.

In a general oxidation procedure, a 50 ml two neck round bottomed flask was charged with vanadyl acetate [19] (72 mg), a nitrile (4 mmol), in dry dichloromethane (7 ml) under N_2 atmosphere and one or two equivalents of *t*-BuOOH were then added to the reaction mixture and allowed to stirr further at room temperature for 24 h. The reaction was periodically monitored by thin layer chromatography. After the completion of reaction, the reaction mixture was then washed with distilled water and extracted with dichloromethane. The combined extracts were then concentrated and subjected to column chromatography to get pure peroxo or aroyl cyanides, respectively.

Acknowledgements

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