ELSEVIER

Journal of Molecular Catalysis A: Chemical 103 (1995) L1–L3

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Letter

A new peroxo vanadium catalyst for selective oxidation of aralkenes to benzaldehydes [1]

B.M. Choudary *, P.N. Reddy

Homogeneous Catalysis Discipline, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 23 February 1995; accepted 18 May 1995

Abstract

Unusual reactivity of peroxo vanadium complex for catalytic oxidation of aralkenes to benzaldehydes selectively (>99%) in conjunction with aqueous hydrogen peroxide as an oxidant is described for the first time.

Keywords: Vanadium peroxo complex; Catalytic oxidation; Styrenes; Stilbenes; Benzaldehydes

1. Introduction

The transition metal peroxo complexes can play an important role in catalytic oxidation of hydrocarbons by hydrogen peroxide [1]. With the discovery of bromo peroxidase vanadium(V) containing enzyme which is isolated primarily from marine algae which catalyses the oxidation of halides Br^-, Cl^-, I^- by hydrogen peroxide [2,3], the reactivity of vanadium chemistry received renewed attention. Selective oxidation of aralkenes to benzaldehydes is an important reaction in synthetic organic chemistry. Selective oxidation of olefins to either epoxides or cleavage products failed due to various non-selective radical reactions leading to a large diversity of unidentified products [4–6]. Earlier attempts to achieve stoichiometric oxidation of olefins selectively to aldehydes by vanadium(V) peroxo picolinate complexes such as $VO(O_2)(pic)(H_2O)_2$, $VO(OOBu^t)(dipic)(H_2O)$ and $VO(OOBu^t)(dipic)(HMPT)$ resulted in the formation of a mixture of epoxide and oxidative cleavage products [7]. The non-selectivity to scission products is ascribed to the stability of the vanadium catalyst, attained due to presence of basic ligands on the metal that prevents the cleavage of epoxides to aldehydes. Hence, we designed vanadium complex bearing acidic ligands to explore the oxidation of aralkenes in our study.

The first report of hydroxylation of benzene by peroxo vanadium(V) complex rendered catalytic with the aid of hydrogen peroxide [8] prompted us to reveal our results of oxidation of aralkenes to benzaldehydes using new peroxo vanadium complex, catalytically for the first time with excellent selectivity and high conversions.

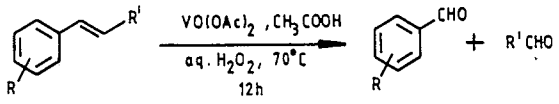
2. Results and discussion

We present here the results that demonstrate the synthetic scope of the new peroxo vanadium com-

* Corresponding author. Tel. (+91-40)673757, fax (+91-40)673387.

[1] I.I.C.T. Communication No. 3300.

1381-1169/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 1381-1169(95)00113-1



Scheme 1.

plex as a catalyst for the clean oxidation of aralkenes to benzaldehydes selectively (>99%). Especially the unique feature is that the aromatic aldehydes formed were not oxidised to the corresponding acids (Scheme 1).

All the styrenes are oxidised smoothly to corresponding aldehydes selectively with excellent yields ranging 86–98%, irrespective of the substituent present on the aromatic ring (Table 1). The yields of the products are comparable to the best system reported so far using expensive ruthenium substituted heteropoly anions for the oxidation of styrenes to benzaldehydes with the aid of sodium periodate as an oxidant[9–11]. However, the oxidation of aliphatic olefins and stilbenes proceeds sluggishly with high selectivity and poor yields.

The salient features of the present reaction

1. This is the first catalytic methodology for the oxidation of olefins selectively with high yield using peroxo vanadium complex with the aid of hydrogen peroxide as an oxidant.
2. Degradation of the catalyst is not observed due to acidic conditions which we used during the reaction.
3. The present methodology is simple and elegant to replace the expensive ozonizer equipment which is widely used in laboratory and industry for the synthesis of aldehydes from aralkenes.
4. This methodology is economical when compared with ruthenium substituted heteropoly anions catalysed oxidation of styrenes to benzaldehydes with the aid of sodium periodate. The latter reaction when conducted with hydrogen peroxide in place of sodium periodate resulted in the non-productive decomposition of hydrogen peroxide to water and dioxygen [9].

Table 1
A new peroxo-vanadium catalysed selective oxidation of aralkenes

Entry	R	R'	Yield (%)
1	H	H	95
2	*p*-CH_3	H	86
3	*o*-CH_3	H	94
4	*m*-NO_2	H	98
5	*p*-Cl	H	92
6	*p*-Br	H	98
7	*p*-OCH_3	NO_2	no reaction
8	*m*-OCH_2Ph	H	92
9	*p*-OAc	H	94
10	*p*-OCH_3	H	91
11	H	Ph	46
12	*p*-OCH_3	Ph	58
13	3,4-$(O)_2CH_2$	Ph	52

All the products were identified by ^{1}H NMR, IR and mass spectrometry.

Vanadyl(IV) acetate [12] is rapidly oxidised by hydrogen peroxide in acetic acid to give red peroxo vanadium complex $VO(O_2)(OAc)_2(H_2O)_2$ (**1**) in situ and in turn oxidises aralkenes to corresponding aldehydes [13] and catalyst (**1**) may be restored by addition of hydrogen peroxide. The necessary prerequisite in this system is slow addition of hydrogen peroxide during the reaction.

The newly designed peroxo vanadium complex bearing acidic ligands i.e acetates are probably playing dual role, one is preventing the catalyst from decomposing to dimer as was the case earlier, so that the reaction can be rendered catalytic and the other one is enhancing the reactivity of the catalyst towards aldehydes.

In conclusion, the successful effort to develop a first catalytic methodology using a new peroxo vanadium catalyst widens the scope of vanadium chemistry for the organic transformations.

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 instruments.

4. Oxidation procedure

In a typical experimental procedure, styrene (2 mmol), vanadyl acetate (36 mg) were taken in 5 ml acetic acid in a 25 ml round bottomed flask and 30% aqueous hydrogen peroxide was added dropwise to the reaction mixture till the brick red colour persists and stirring is continued for 12 h at 70°C. The reaction mixture was treated with saturated sodium hydrogen carbonate solution and extracted with diethyl ether, all the combined extracts were concentrated, dried over anhydrous sodium sulphate and subjected to column chromatography; yield 95% (201 mg).

Acknowledgements

We thank UGC for financial support to PNR.

References

[1] R.A. Sheldon and J.K. Kochi, Metal Catalysed Oxidation of Organic Compounds, Academic Press, New York, 1981.
[2] H. Vilter, Phytochemistry, 23 (1984) 1387.
[3] A. Butler and J.V. Walker, Chem. Rev., 93 (1993) 1937.
[4] R.S. Drago, B.B. Cordon and C. Bornes, J. Am. Chem. Soc., 108 (1986) 2453.
[5] F. Pappo, P.S. Allen, P.M. Lemieux and W.S. Johnson, J. Org. Chem., 21 (1956) 478.
[6] K.B. Sharpless, A.Y. Ternishi and J.E. Backvall, J. Am. Chem. Soc., 99 (1977) 3120.
[7] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fisher and R. Weiss, J. Am. Chem. Soc., 105 (1983) 3101.
[8] M. Bianch, M. Bonchio, V. Conte, F. Coppa, F.D. Fura, G. Modena, S. Moro and S. Standen, J. Mol. Catal., 83 (1993) 107.
[9] R. Neumann and C. Abu-gnim, J. Am. Chem. Soc., 112 (1990) 6025.
[10] R. Neumann and C. Abu-gnim, J. Chem. Soc., Chem. Commun., (1989) 1324.
[11] E. Steckhan and Kandzia, Syn. Lett., 2 (1992) 139.
[12] F.A. Cotton, Inorg. Syn., 13 (1972) 181.
[13] A. Butler, M.J. Clague and G.E. Meister, Chem. Rev., 94 (1994) 625.