

Oxidations of Benzyl Alcohol by Hydrogen Peroxide in the Presence of Complexed Peroxonioibium(v) Species†

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The influence of ligands around peroxo niobium complexes and of the ratio of oxygen-source substrates towards the efficiency of the niobium(v)-catalysed oxidation of benzyl alcohol to benzaldehyde by hydrogen peroxide has been analysed: the use of ligands such as phenylphosphonic acid and 2,2'-bipyridyl associated with peroxoniobate gave efficient systems.

The oxidation of alcohols to aldehydes or ketones is an important transformation in organic synthesis.¹ Oxidation of secondary alcohols to ketones can be carried out with hydrogen peroxide and transition metal complexes of Mo,^{2–4} V,⁵ Ti⁶ and Cr.^{7,8} The oxidative ability towards the alcoholic function of a series of peroxomolybdenum complexes has been evaluated.^{9,10} Recently we became involved in the chemistry of peroxoniobium(v) complexes in the oxidation of alcohols and olefins. In the present work, systems comprising peroxoniobium(v) species complexed with phenylphosphonic acid and 2,2'-bipyridyl have been checked for the catalytic oxidation of benzyl alcohol by hydrogen peroxide.

In all experiments the catalytic systems were formed *in situ* by mixing appropriate amounts of peroxoniobium(v) species and ligands. The reactions were carried out under biphasic conditions where the solvent was 1,2-dichloroethane and the oxidant was an aqueous solution of hydrogen peroxide. The results presented in Table 1 show that in the reaction without catalyst (entry 1) the yield of benzaldehyde was <0.1%, while with NbCl₅ and without ligand the yield of benzaldehyde after 9 h was 13.9% (entry 2). In the presence of the ligand phenylphosphonic acid and an excess of H₂O₂ in relation to benzyl alcohol, we also achieved a higher turnover (entry 6) than that reported in the literature^{9,11} for other peroxo systems in the oxidation of the same alcohol. In the presence of 2,2'-bipyridyl (entry 10) we similarly achieved a higher turnover, but an excess of H₂O₂ decreased the conversion of benzyl alcohol (entries 9 and 11). In all reactions the

main product was the benzaldehyde, but in some cases, with an excess of H₂O₂, we verified the presence of benzoic acids (entries 3, 4, 6 and 11).

In conclusion, this investigation has shown that complexes of niobium, together with 2,2'-bipyridyl is effective for the oxidation of benzyl alcohol to benzaldehyde in excellent yield without oxidation to benzoic acid.

Experimental

Benzyl alcohol and 1,2-dichloroethane (DCE) was purified by distillation. Phenylphosphonic acid, tetrabutylammonium hydroxide and 2,2'-bipyridyl were commercially available, high-purity products (Aldrich) and were used as received. Hydrogen peroxide solution [30% (w/w)] was purchased from Peróxidos do Brasil S/A and niobium pentachloride from Companhia Brasileira e mineração (CBMM).

Typical Experimental Procedure (see Table 1 for Times and Amounts).—In a round-bottomed flask was added sequentially 1,2-dichloroethane (50 ml), benzyl alcohol (1 mmol), NbCl₅, the ligand, tetrabutylammonium hydroxide and aqueous H₂O₂ (30% w/w). The oxidations were run at 40 °C. Aliquots of the reaction were withdrawn at various times, and the amount of the product were determined by GC analysis on an SE-54 column after reactions with triphenylphosphine to consume the excess of H₂O₂.

We gratefully acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Universitária José Bonifácio (FUJB) for financial support.

Received, 28th August 1996; Accepted, 18th November 1996
Paper E/6/05944I

Table 1 Oxidation of benzyl alcohol (1 mmol) by hydrogen peroxide in the presence of peroxoniobium(v) species complexed with phenylphosphonic acid (PPA) and 2,2'-bipyridyl (BP)

Entry	Catalytic system (mmol) ^a	H ₂ O ₂ (mmol)	Time (t/h)	Conversion of alcohol (%)	Selectivity (%)		Turnover ^b
					Benzoic acid	Benzaldehyde	
1	—	1	30	0.1	—	100	—
2	NbCl ₅ + 1 equiv. QOH (0.25)	1	9	13.9	—	100	0.56
3	NbCl ₅ + 1 equiv. PPA + 1 equiv. Q ⁺ OH (0.1)	1	2	15.9	1.2	98.8	1.59
4	NbCl ₅ + 1 equiv. Q ⁺ OH + 1 equiv. PPA	2	2	25.5	4.8	95.2	2.55
5	NbCl ₂ + 1 equiv. PPA + 1 equiv. Q ⁺ OH (0.25)	1	5	53.9	—	100	2.16
6	NbCl ₅ + 1 equiv. QOH + 1 equiv. PPA (0.25)	2	2	84.5	5.6	94.4	3.38
7	NbCl ₅ + 1 equiv. PPA + 1 equiv. Q ⁺ OH (0.50)	1	5	86.6	—	100	1.73
8	NbCl ₅ + 1 equiv. BP (0.10)	1	2	13.5	—	100	1.35
9	NbCl ₅ + 1 equiv. BP (0.10)	2	2	7.5	—	100	0.75
10	NbCl ₅ + 1 equiv. BP (0.25)	1	2	82.4	—	100	3.3 ^c
11	NbCl ₅ + 1 equiv. BP (0.25)	2	2	19.0	6.2	93.8	0.76

^aQOH = Tetrabutylammonium hydroxide. ^bDefined as $T = \text{mmol products}/\text{mmol catalyst}$. ^cA value of 1.92 is reported in ref. 9.

^dReaction carried out in DCE at 40 °C.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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