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ScienceDirect
Tetrahedron Letters 47 (2006) 8017–8019
Tetrahedron Letters

Selective oxidation of sulfides to sulfoxides using a silica immobilised vanadyl alkyl phosphonate catalyst

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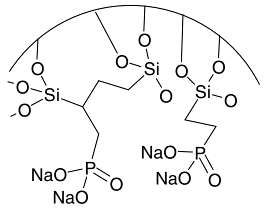
Received 31 July 2006; revised 7 September 2006; accepted 15 September 2006
Available online 2 October 2006

Abstract—A range of sulfides can be selectively oxidised to the corresponding sulfoxides in good yields using catalytic quantities of immobilised vanadyl, cobalt or nickel alkyl phosphonates and the reoxidant sodium bromate or vanadyl alkyl phosphonate with *tert*-butyl hydroperoxide or aqueous hydrogen peroxide as oxidants.

The selective oxidation of sulfides to sulfoxides is of interest because of the importance of sulfoxides as synthetic intermediates in organic synthesis.[1] Of particular relevance to this paper are a number of recent studies on silica supported catalysts. These include several with immobilised titanium, TS-1, Ti-beta[2,3] and Ti-MCM-41[4] and Ti–SiO_2,[5] immobilised chiral salen copper and manganese complexes,[6] immobilised ammonium tungstate,[7] immobilised vanadyl acetoacetonate[8] and micelle directed polyoxometallate assemblies.[9] Some of the challenges include oxidation of bulky sulfides,[3] controlling over-oxidation to the sulfone[4,7] and leaching of catalytic metal[5] in addition to the challenge of accomplishing this with environmentally friendly oxidants.

We have reported a range of catalytic oxidation studies utilising silica immobilised metal phosphonates as catalysts including allylic oxidation, with the Co(II)/TBHP system (TBHP is *tert*-butyl hydroperoxide), allylic alcohol oxidation (Co(II) or VO/TBHP) and primary and secondary alcohol oxidation (Ce(IV)/$NaBrO_3$).[10–13] Most recently, we reported on catalytic sulfide oxidation using the Ce(IV) derivative of **1** (obtained from Na**1**) with $NaBrO_3$ or TBHP as reoxidants, where the catalyst was derived from material Na**1** with composition $\{[O_2Si]_3[O_{3/2}Si(CH_2)_2PO(ONa)_2]_{0.5}[O_{3/2}SiCH(CH_2PO(ONa)_2)CH_2CH_2SiO_{3/2}]_{0.5}\}$.[14] In this follow-up letter, we report on further sulfide oxidation studies using the vanadyl derivative of **1** with three different co-oxidants.



Na**1**

In an earlier work, we reported that the selectivities observed for heterogeneous oxidation of sulfides using the Ce(IV)**1**–$NaBrO_3$ system compare extremely well with reported selectivities for other heterogeneous catalysts and we indicated that this system is more selective than the corresponding Ce(IV)**1**–TBHB system.[14]

In the current study, we initially screened three different additional Metal**1**–$NaBrO_3$ catalysts (VO**1**, Co**1** and Ni**1**) for the oxidation of thioanisole and then selected VO**1** for assessment with a wider range of substrates and two additional oxidants (TBHP and H_2O_2). Typical procedures for the preparation of Metal**1** catalysts and for the oxidation reactions discussed are given in reference notes.[15–18] The results of the oxidation reactions are given in Table 1.

The Metal**1**–$NaBrO_3$ catalysts (metal = VO, Co(II), Ni(II)) were found to be selective and with the exception of Co**1**, more active than the Ce**1**–$NaBrO_3$ system, for

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Keywords: Sulfide; Sulfoxide; Oxidation; Vanadyl; Phosphonate; Sodium bromate; *tert*-butyl hydroperoxide; Aqueous hydrogen peroxide; Silica; Immobilised reagents.

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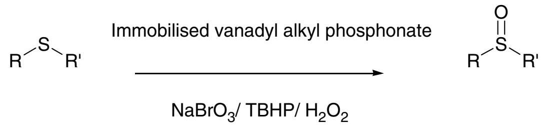
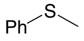
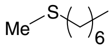
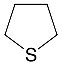
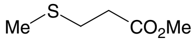
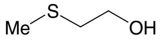
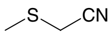
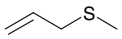
doi:10.1016/j.tetlet.2006.09.065

Table 1.



Substrate[a]	% Sulfoxide[b] (Cat)$NaBrO_3$	% Sulfoxide (VO1)[h]TBHP	% Sulfoxide (VO1)[k]H_2O_2
	99[c,d]	99[i]	99[l]
	70[e,f]	99	99
	99[e]	99	99
	99[e,g]	99[j]	99
	99[e]	99	99
	99[e,g]	99	99
	99[e]	70[f]	99

[a] See Ref. 14 for Ce1–$NaBrO_3$ and Ce1–TBHP systems.

[b] Conversions were ~99% by proton NMR; only trace amounts of residual sulfide were observed and oxidations were generally selective with only trace amounts of sulfone seen in most cases. Run time was 1 h at room temperature unless otherwise stated.

[c] 0.03 g catalyst, 1 mmol substrate, 1.5 mmol $NaBrO_3$ in CH_3CN (3 mL), H_2O (0.5 mL), room temperature, 1 h (**VO1**), 4 h (**Ni1**), 1 h 40 °C (**Co1**); inactive in the absence of sodium bromate.

[d] Recycled three times, **VO1**, 4% over-oxidation in the second recycle.

[e] Catalyst is **VO1**.

[f] 30% over-oxidation to sulfone observed.

[g] Reaction time 2 h.

[h] 0.03 g VO catalyst, 1 mmol substrate, 5 mL acetonitrile, 2 equiv TBHP 70% in water, 1 h, room temperature.

[i] Recycled three times without change; no conversion in the absence of TBHP.

[j] 2 h, recycled three times without change.

[k] 0.03 g **VO1** catalyst, 1 mmol substrate, 5 mL acetonitrile, 2 equiv H_2O_2 (30% in water) at room temperature, 1 h.

[l] Recycled three times without change.

the oxidation of thioanisole. For the Co**1** catalyst, the conversion of sulfide to sulfoxide at room temperature was 80% after 17 h but a complete conversion to the sulfoxide was achieved in 1 h at 40 °C. It is noteworthy that the related Ce**1**–$NaBrO_3$ system was generally less active at room temperature and heating at 30–50 °C was required. The vanadyl catalyst **VO1** showed ~4% over-oxidation on the second and third recycles. The Metal**1** catalysts were found to be inactive if the reoxidant bromate was excluded. On the basis of performance in this initial study, the **VO1**–$NaBrO_3$ system was screened further with a wider range of substrates and **VO1** itself with 70% aqueous TBHP and 30% aqueous H_2O_2 as oxidants. For the other sulfide substrates examined with **VO1**–$NaBrO_3$, selective oxidation to the sulfoxide was observed, except for heptyl methylsulfide where there was substantial over-oxidation to the sulfone. In contrast, the analogous cerium catalysed reaction run at 40 °C was ~96% selective for the sulfoxide.[13] For the **VO1**–TBHB catalyst at room temperature substantial over-oxidation to the sulfone was observed for 3-methylthio-1-propene, (no epoxide formed) but selectivity for sulfoxide prevailed under these conditions in the other cases including heptyl methyl sulfide. The **VO1**–TBHB catalyst was recycled three times without loss in activity using methyl 3-methylsulfinylmethylpropionate. With the **VO1**–H_2O_2 system, all five substrates had ~99% selectivity for the sulfoxide. The **VO1**–H_2O_2 catalyst was successfully recycled three times with thioanisole as the substrate.

The **VO1** catalyst has generally shown an impressive activity (with no detectable leaching of metal)[19] for the selective oxidation of sulfides with the three co-oxidants used and the results with environmentally clean 30% aqueous hydrogen peroxide are particularly noteworthy.

References and notes

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15. Preparation of Metal**1** materials. The metal was introduced as $VOSO_4{\cdot}5H_2O$, $M(NO_3)_2{\cdot}6H_2O$, M = Co, Ni; $Cu(NO_3)_2{\cdot}5H_2O$. Metal**1**, was prepared by treating an aqueous suspension of the disodium phosphonate material, Na**1**, with an aqueous solution of metal compound (such that phosphonate: metal complex = 1:2). The solids obtained were filtered, washed with copious amounts of water and then with ether and finally dried at 100 °C/0.01 Torr. Metal loading (mmol g^{-1}) V 1.08, Co, 1.2 Ni, 1.3 was measured by determining the quantity of metal released from a known weight of material treated with conc. nitric acid using atomic absorption spectroscopy.
16. Typical procedures using the Metal**1**–$NaBrO_3$ system. The catalyst and sulfide (see Table 1 for quantities) were added to acetonitrile (3 mL) and then sodium bromate (0.23 g) and water (0.5 mL) were then added. This mixture was stirred at the temperature and for the time indicated in Table 1. The reaction was followed by TLC. The catalyst was separated by filtration and washed with ethyl acetate. The combined filtrate and ethyl acetate washings were then washed with water and the organic phase was

separated and dried over magnesium sulfate. The product was obtained after removal of the solvent and the conversion was assessed by NMR.

17. In each case, the quantity of $NaBrO_3$ used (1.5 mmol) represents a large excess over that required to reoxidise the metal following the oxidation of 1 mmol of sulfide (assuming that sodium bromide is formed in the process).
18. Typical procedure using the VO**1**–TBHB or VO**1**–H_2O_2 system. To a solution of sulfide in acetonitrile (5 mL) was added the catalyst followed either by a 70% aqueous solution of *tert*-butyl hydroperoxide or a 30% aqueous solution of hydrogen peroxide (see Table 1 for quantities). This reaction mixture was stirred at the temperature and for the time indicated and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and washed with diethyl ether. The combined organic fractions were washed with sodium sulfite (10% aq 10 mL), extracted with diethyl ether and the extract dried over magnesium sulfate. The solvent was evaporated to give the products and conversion was assessed without further purification by the inspection of the 270 MHz proton NMR spectra (account was taken of the relative integrations of resonances due to the sulfide, sulfoxide and sulfone as appropriate).
19. Filtrates taken after 30 min at the reaction temperature showed no further conversion up to 24 h.