



Oxidation of alcohols using cerium(IV) alkyl phosphonate modified silica

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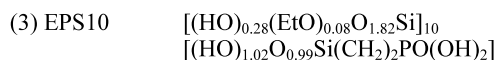
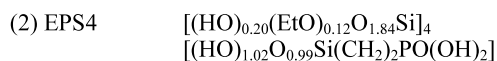
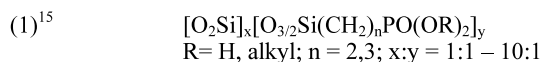
Abstract—The oxidation of a range of alcohols to ketones or carboxylic acids proceeds in good yield using catalytic quantities of cerium(IV) phosphonate modified silica and sodium bromate as the re-oxidant. © 2003 Elsevier Science Ltd. All rights reserved.

The oxidation of primary and secondary alcohols to carboxylic acids and ketones is a very important organic transformation that is extensively used in the manufacture of a wide range of products. Traditionally, stoichiometric or larger quantities of reagents based on manganese or chromium have been utilised for this transformation. Difficult work-up conditions and environmentally hazardous manganese and chromium residues are some of the problems associated with their use. With the widely accepted drive towards more sustainable technologies—Green Chemistry—there is an urgent need for catalytic oxidation technologies. Of particular importance is heterogeneous catalysis, as it possesses many advantages including ease of recovery and recycling and the suitability for continuous processing.

A variety of mainly homogeneous and a few heterogeneous methods for the oxidation of alcohols have been

reported. Swern and Oppenauer methodologies are two well-known processes. Nitroxyl radicals¹ such as 2,2,6,6-tetramethyl piperidinyloxy (TEMPO) are effective catalysts for the oxidation of alcohols. Dimethyldioxirane² is an effective reagent that generally oxidises secondary faster than primary alcohols. A number of *N*-halogenated reagents³ have also been reported to show similar selectivity. Soluble hypervalent iodine(V) derivatives⁴ such as periodinane and *o*-iodoxybenzoic acid are mild reagents for the oxidation of both primary and secondary alcohols. Molybdenum-catalysed alcohol oxidations⁵ utilising 30% aqueous hydrogen peroxide, with tetrabutyl ammonium chloride as a phase transfer reagent, have been reported. Ruthenium complexes⁶ with molecular oxygen are also effective at oxidising alcohols. Liquid phase oxidations of alcohols⁷ using molecular oxygen, a supported platinum group metal catalyst and water as solvent proceed in high yield particularly for water soluble alcohols.

Investigations began in the 1960s into the use of Ce(IV) reagents for the oxidation of alcohols. Utilising stoichiometric quantities of either cerium(IV) sulphate or cerium ammonium nitrate (CAN) the oxidation of benzylic alcohols⁸ and cyclopropyl methanol⁹ to their corresponding aldehydes could be conducted in good yields. However oxidation of other substrates¹⁰ such as linear or bicyclic alcohols, hydroxy ketones, aryl alkyl alcohols and glycols resulted in fragmentation and/or oxidation to varying degrees. Ho reported¹¹ that catalytic quantities of CAN, in the presence of the re-oxidant sodium bromate, could be used to oxidise benzylic alcohols to their corresponding aldehydes. This system was further explored by Oshima who reported¹² the oxidation of a variety of secondary alcohols including bicyclic and linear alcohols as well as benzoin to their corresponding ketones without fragmentation.



Scheme 1.

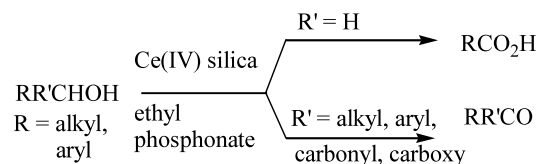
Keywords: oxidation; alcohols; ketones; carboxylic acids; cerium; phosphonate; silica; immobilised reagents.

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We recently reported^{13,14} the synthesis and characterisation of the first examples of phosphonate and phosphonic acid modified silicas (1)¹⁵ (see Scheme 1). We are currently exploring their use as acid catalysts. The ethyl phosphonate modified silica materials (EPS) prepared to date have Q:T ratios in the range 1:1 to 10:1. In all cases we found the T components to have ca. 66% condensation and Q ca. 90%. In this work two EPS materials¹³ EPS4 and EPS10 were employed with average formulae (2) and (3) (see Scheme 1). Average formulae were derived as previously described.¹³

A range of metal derivatives, including vanadyl,¹⁶ of these EPS and propyl phosphonic acid modified silicas, PPS, have been prepared and their chemistry and structural characteristics are currently being investigated. In this paper we wish to report our initial work on the catalytic oxidation of alcohols utilising cerium(IV) immobilised on the EPS systems (2) and (3).

As far as we are aware no cerium(IV) derived heterogeneous reagents have been reported for the oxidation of alcohols. In addition we could find no reports of cerium phosphonate compounds. The cerium(IV) ethyl phosphonate modified silicas, CeEPS, were prepared by treating an aqueous suspension of the disodium EPS with an aqueous solution of cerium ammonium nitrate. The yellow solid was filtered, washed with copious amounts of water and then with ether and finally dried at 100°C at 0.01 Torr. As illustrated in Scheme 2 and in Table 1 a range of alcohols can be oxidised to ketones or carboxylic acids using the CeEPS catalysts.



Scheme 2.

Table 1.

Alcohol (1 mmol)	Product	Catalyst ^a (mmol) Ce (IV)	Time (h)	Isolated yield (%)
1-Phenyl-1-propanol	1-Phenylpropan-1-one	CeEPS4-0.027	48	99
1-Phenyl-1-propanol	1-Phenylpropan-1-one	CeEPS10-0.033	48	99
1-Phenyl-1-propanol	1-Phenylpropan-1-one	CeEPS4-0.027	48	95 ^c
1-Phenyl-1-propanol	1-Phenylpropan-1-one	CeEPS4-0.027	2	18 ^d
1-Phenyl-1-propanol	1-Phenylpropan-1-one	CeEPS4-0.027	48	18 ^c
Benzyl alcohol	Benzoic acid	CeEPS10-0.033	24	93
Benzyl alcohol		0 ^b	24	0
Benzyl alcohol	Benzoic acid	CeEPS10-0.033	24	89 ^c
4-Methylbenzyl alcohol	4-Methylbenzoic acid	CeEPS10-0.033	24	92
4-Fluorobenzyl alcohol	4-Fluorobenzoic acid	CeEPS10-0.033	24	93
2-Hexanol	2-Hexanone	CeEPS4-0.027	26	98
2-Octanol	2-Octanone	CeEPS4-0.027	24	99
2-Octanol	2-Octanone	CeEPS10-0.033	24	99
2-Octanol		0 ^b	48	0
2-Dodecanol	2-Dodecanone	CeEPS4-0.027	24	99
2-Dodecanol		0 ^b	48	0
2-Dodecanol	2-Dodecanone	CeEPS10-0.033	22	99
Menthol	Menthone	CeEPS10-0.033	72	54
Cyclohexanol	Cyclohexanone	CeEPS4-0.027	48	62
4-Chlorophenyl-4-methylphenyl methanol	4-Chlorophenyl, 4-methylphenyl methanone	CeEPS10-0.033	48	99
2-Hydroxy-1,2-diphenyl ethanone	1,2-Diphenyl ethanedione	CeEPS10-0.033	52	99
Mandelic acid	Phenylglyoxylic acid	CeEPS4-0.027	52	98
Mandelic acid	Phenylglyoxylic	CeEPS10-0.033	48	98
1-(2-Pyridinyl)-2-phenyl ethanol	1-(2-Pyridinyl)-2-phenyl ethanone	CeEPS10-0.033	48	92
1-Octanol	Octanoic acid	CeEPS4-0.027	29	83
1-Octanol	Octanoic acid	CeEPS10-0.033	31	37
1-Decanol	Decanoic acid	CeEPS4-0.027	29	81
1-Decanol	Decanoic acid	CeEPS10-0.033	30	50

^a All reactions were performed with 2 mmol sodium bromate, 40 mg CEPS4 and 80 mg CEPS10 taken.

^b Reaction in absence of CeEPS catalyst.

^c Average of three separate runs using the same catalyst. The catalyst was filtered, washed well with water and with diethyl ether and then dried at 100°C at 0.01 Torr.

^d The hot mixture was filtered very quickly at its reaction temperature. The reaction mixture at this point contained 18% 1-phenylpropan-1-one and the remainder was starting alcohol, as determined by ¹H NMR analysis.

^e The filtered reaction mixture plus additional sodium bromate from the entry above was refluxed for a further 48 h. No further reaction had occurred as indicated by ¹H NMR analysis.

A typical procedure¹⁷ involves the gentle reflux of a mixture containing the catalyst at concentrations of 2.7–3.3 mol% Ce(IV)¹⁸ and sodium bromate as the re-oxidant in an acetonitrile-water solvent system.

Although neither the procedure nor the catalyst systems have been optimised, yields are very good and the catalyst can be effectively recycled, as the examples with 1-phenyl-1-propanol and benzyl alcohol demonstrate. It has been reported¹¹ that sodium bromate alone does not oxidise alcohols. However, in order to confirm this finding we investigated its reaction with benzyl alcohol, 2-octanol and 2-dodecanol, respectively. Only starting alcohols were obtained even after prolonged reaction times. To check for leaching, the catalyst was filtered, at the reaction temperature, from the oxidation of 1-phenyl-1-propanol after two hours and the filtrate was allowed to react further. No further oxidation was observed. This suggests that oxidation is occurring at the immobilised cerium(IV) site.

Fragmentation and dehydration were observed side reactions¹⁰ when stoichiometric quantities of cerium(IV) ammonium nitrate or sulphate were used with alcohols containing aryl, heteroaryl or a range of other functionalities. Reaction using the CeEPS catalysts with benzoin, mandelic acid and 1-phenyl-1-propanol gave the corresponding ketones in very high yield. No fragmentation or dehydration products were observed in these cases. Oxidation of a number of benzylic alcohols utilising the CeEPS catalysts afforded the corresponding carboxylic acids. The presence of the respective aldehydes¹⁹ was observed during the reaction. Interestingly it has been reported⁸ that reaction of benzyl alcohol with stoichiometric quantities of the homogeneous reagent CAN gives only benzaldehyde. The CeEPS catalysts can also oxidise primary alcohols although at a slower rate.

In conclusion we have demonstrated that a new catalytic system based on immobilised cerium(IV) phosphonates can effectively oxidise a range of alcohols to either ketones or carboxylic acids in very high yield.

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17. Typical procedure. The alcohol dissolved in acetonitrile (4 ml) was added to the CeEPS catalyst. The mixture was stirred and then sodium bromate (0.3 g, 2 mmol) and water (0.5 ml) was added and the mixture was gently refluxed under an atmosphere of nitrogen. On completion the catalyst was filtered and washed well with ether and water. The filtrate was separated, dried and concentrated under reduced pressure.
18. Ce⁺⁴ concentration was determined by titration after the metal ion was liberated by treatment of the CeEPS with concentrated nitric acid.
19. The cerium(IV) immobilised silica phosphonate catalysts oxidises benzaldehyde to benzoic acid.