polymer report

Polymer-supported ceric(IV) catalyst: 1. Catalytic ring opening of epoxides

B. Tamami*, N. Iranpoor* and M. A. Karimi Zarchi
Chemistry Department, Shiraz University, Shiraz, Iran
(Received 17 June 1992; revised 10 October 1992)

Poly(vinyl pyridine)-supported ceric(IV) complex can be easily prepared. It catalyses nucleophilic ring opening of epoxides in alcohols under mild conditions with high regio- and stereoselectivity. The reaction work-up is easy and the catalyst can be reused several times without its activity changing appreciably. Regeneration of the catalyst is easily achieved.

(Keywords: polymer-supported ceric(IV) catalyst; epoxide ring opening)

INTRODUCTION

Ceric(IV) salts have been extensively used for the oxidation of different organic compounds[1]. There are reports in the literature that ceric(IV) has also been used in catalytic amounts in the dual oxidant system, ceric ammonium nitrate/$NaBrO_3$, for oxidation of different compounds[2–4].

Recently, it was reported that, as one-electron transfer catalysts, several Ce(IV) species such as ceric ammonium nitrate, ceric pyridinium nitrate and ceric sulfate can catalyse nucleophilic ring opening reactions of epoxides under mild conditions with high regio- and stereoselectivity[5–7]. Ring opening with the help of these catalysts could eliminate some of the disadvantages usually encountered in other methods, such as high acidity[8,9] unsatisfactory regioselectivity[10], and inconvenient handling requirements[10,11].

The study of polymer-supported catalysts has been a rapidly developing and important field of polymer science[12,13]. However, to the best of our knowledge there is only one report in the literature of a polymer-supported ceric(IV) compound, and that is ceric(IV)-impregnated Nafion used as a catalyst in oxidation of alcohols with hydroperoxides[14].

In this report we introduce the preparation and use of poly(vinyl pyridine)-supported ceric(IV) complex as a catalyst for regio- and stereoselective ring opening alcoholysis of epoxides.

EXPERIMENTAL

Crosslinked poly(2-vinyl pyridine) (2% divinylbenzene) was purchased from Fluka A.G. The reactions were monitored by gas chromatography and on completion of the reaction the pure products were obtained by simple filtration and washing with alcohol. Products were characterized by comparison of their i.r. and/or n.m.r. spectra and physical data with those of authentic samples. All yields refer to the isolated products.

Preparation of poly(2-vinyl pyridinium)ceric nitrate, $Ce[(PVP.H)_2(NO_3)_6]$

To a suspension of poly(2-vinyl pyridine) (1 g) in cold concentrated nitric acid (30 ml), a nitric acid solution of ceric hydroxide (20 mmol) was added slowly with stirring. Stirring was continued for 24 h when the yellow–orange precipitate was filtered, washed with methanol (5 x 20 ml) and dried in vacuum at 50°C, to give 2.33 g of ceric compound. The capacity was determined to be 1.11 ± 0.02 mmol ceric(IV) per gram of polymer.

General procedure for ring opening of epoxides in alcohols

To a solution of epoxide (1 mmol) in the appropriate alcohol (3–5 ml), polymer-supported ceric(IV) complex catalyst (0.1–0.4 mmol) was added and stirred at room temperature or under reflux. The reaction was monitored by gas chromatography. After completion of the reaction, the suspension was filtered and washed with alcohol. Solvent was evaporated and the pure product obtained in high yield (*Table 1*).

Regeneration of the polymer-supported ceric(IV) catalyst

To a cream-coloured suspension of the used polymer-supported ceric complex (1 g) in nitric acid (30 ml), sodium bromate (0.15 g) was added and stirred for 5 min. A yellow–orange precipitate formed which was then filtered and washed several times with a minimum amount of methanol and dried in vacuum.

RESULTS AND DISCUSSION

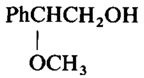
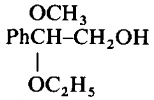
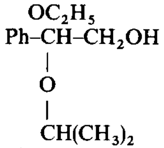
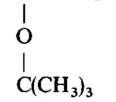
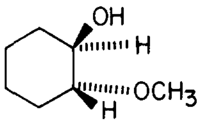
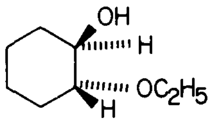
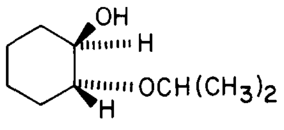
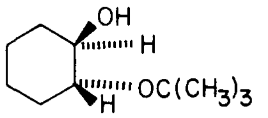
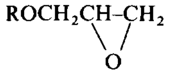
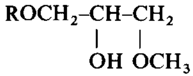
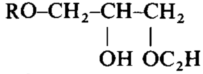
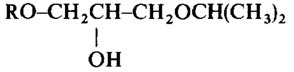
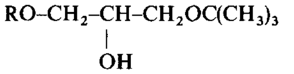
Poly(2-vinyl pyridinium)ceric nitrate is easily prepared by reaction of ceric hydroxide and poly(2-vinyl pyridine) in nitric acid. This polymer-supported ceric(IV) catalyst in 0.1–0.4 molar ratios can catalyse regio- and stereoselective ring opening alcoholysis of different epoxides (*Table 1*). The main advantage of this polymeric ceric(IV) catalyst compared to the unsupported monomeric analogues, such as ceric ammonium nitrate and pyridinium ceric nitrate, is that ceric ions are tightly bound to the polymeric bed. The final reaction product can be simply filtered and separated from the catalyst without the need for a further chromatographic step. In addition, the polymeric catalyst can be reused at least five to seven times without losing its activity appreciably. The catalyst can be restored to its original activity by

---

*To whom correspondence should be addressed

0032-3861/93/092011-03

Table 1 Reactions of epoxides with alcohols catalysed by polymer-supported ceric(IV) complex

Epoxide	Solvent	Mole ratio, catalyst/ substrate[a]	Time[a] (min)	Isolated yield[a] (%)	Products
Styrene oxide	CH_3OH	0.1 (0.2)	10 (50)	98 (87)	 $\mathrm{Ph\underset{OCH_3}{CH}CH_2OH}$
	C_2H_5OH	0.1 (0.2)	30 (50)	95 (86)	 $\mathrm{Ph\underset{OC_2H_5}{CH}{-}CH_2OH}$
	$(CH_3)_2CHOH$	0.2[b] (0.2)	195 (120)	90 (80)	 $\mathrm{Ph{-}\underset{O{-}CH(CH_3)_2}{CH}{-}CH_2OH}$
	$(CH_3)_3COH$	0.4[b] (0.2)	420 (120)	85 (78)	 $\mathrm{Ph{-}\underset{O{-}C(CH_3)_3}{CH}{-}CH_2OH}$
Cyclohexene oxide	CH_3OH	0.1 (0.1)	10 (35)	95 (89)	
	C_2H_5OH	0.1 (0.2)	45 (35)	95 (89)	
	$(CH_3)_2CHOH$	0.2[b] (0.4)	240 (50)	89 (90)	
	$(CH_3)_3COH$	0.4[b] (0.6)	420 (50)	92 (80)	
	CH_3OH	0.1 (0.6)	210 (180)	92 (85)	 $\mathrm{ROCH_2{-}\underset{OH}{CH}{-}\underset{OCH_3}{CH_2}}$
	C_2H_5OH	0.1[b] (0.6)	195 (180)	98 (77)	 $\mathrm{RO{-}CH_2{-}\underset{OH}{CH}{-}\underset{OC_2H_5}{CH_2}}$
	$(CH_3)_2COH$	0.2[b] (0.8)	180 (180)	96 (80)	 $\mathrm{RO{-}CH_2\underset{OH}{CH}{-}CH_2OCH(CH_3)_2}$
	$(CH_3)_3COH$	0.4[b] (0.8)	720 (190)	96 (80)	 $\mathrm{RO{-}CH_2{-}\underset{OH}{CH}{-}CH_2OC(CH_3)_3}$
R: $CH_2=CH{-}CH_2$					

[a] Values in parentheses: reactions catalysed by ceric pyridinium nitrate[7]

[b] The reaction was performed under reflux

treating it with a small amount of sodium bromate in nitric acid.

As shown in the table, the efficiency of the polymeric catalyst is appreciably more than that of the unsupported monomeric analogue when lower alcohols are used as solvents. This can probably be attributed to the higher local concentration of ceric(IV) species inside the pores. With higher alcohols the efficiency becomes less, probably due to the steric factor and also to the lower degree of swelling of the polymer in these solvents.

CONCLUSION

Polymeric ceric(IV) catalyst exhibited good catalytic activity in the regio- and stereoselective ring opening alcoholysis of epoxides. Its use has advantages over the use of unsupported monomeric analogues due to easier work-up, reuse, higher efficiency for lower alcohols and easy regeneration. Application of this polymeric catalyst in other nucleophilic ring opening reactions of epoxides is under investigation.

ACKNOWLEDGEMENT

The authors are grateful to Shiraz University Research Council for the partial support (no. 69-SC-639342) of this work, and to Professor H. Firouzabadi and Dr H. Parham for helpful discussions.

REFERENCES

1 Ho, T. L. *Org. Synth. Oxid. Met. Compd* 1986, 569
2 Ho, T. L. *Synthesis* 1978, **12**, 936
3 Olah, A., Gupta, B. G. and Fung, P. *Synthesis* 1980, **11**, 897
4 Tomioka, H., Oshima, K. and Nozaki, H. *Tetrahedron Lett.* 1982, **23**, 539
5 Iranpoor, N. and Mohammadpour Baltork, I. *Synth. Commun.* 1990, **20**, 2789
6 Iranpoor, N., Mohammadpour Baltork, I. and Shiriny Zardaloo, F. *Tetrahedron* 1991, **47**, 9861
7 Iranpoor, N. Personal communication
8 Winstein, S. and Henderson, R. D. *J. Am. Chem. Soc.* 1943, **65**, 2190
9 Olah, G. A., Fung, A. P. and Meider, D. *Synthesis* 1981, **4**, 280
10 Posner, G. H., Rogers, D. Z., Kinzig, C. H. and Gurria, G. M. *Tetrahedron Lett.* 1975, **42**, 3597
11 Otera, J., Yashinaga, Y. and Hirakama, K. *Tetrahedron Lett.* 1985, **27**, 3219
12 Hodge, P. and Sherrington, D. C. 'Polymer-Supported Reactions in Organic Chemistry', Wiley-Interscience, New York, 1980
13 Pittman Jr, C. U. in 'Comprehensive Organometallic Chemistry', Vol. 8, Pergamon, Oxford, pp. 553–611
14 Kanemoto, S., Saimato, H., Oshima, K. and Nozaki, H. *Tetrahedron Lett.* 1984, **25**, 3317