J. Chem. Research (S), 1999, 572–573†

Epoxidation of Alkenes using Equimolar Levels of *t*-BHP Catalysed by Polybenzimidazole (PBI)-supported Molybdenum(vi)†

Salla-M. Leinonen and David C. Sherrington*

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK

Epoxidation of cyclohexene, styrene and 4-vinylcyclohexene using equimolar levels of *tert*-butylhydroperoxide (*t*-BHP) as the oxidant and a polybenzimidazole-supported molybdenumn(vi) catalyst (PBI.Mo) can be achieved in moderate to good yields (50–70%) by appropriate choice of conditions.

For industrial purposes the maximum utilisation of raw materials in any chemical process is important both economically and environmentally.[1] Selective epoxidation of alkenes under conditions where an excess of alkene is used is fine for a large-scale commodity chemical process utilising a recycling loop,[2] but this is not appropriate for speciality alkenes in small scale pharmaceutical chemical syntheses. Here it would be highly desirable to be able to use equimolar ratios of alkene and the oxidant to achieve good utilisation of the alkene and the oxidant. It has been reported that epoxidations at high hydroperoxide to alkene ratios yield relatively low conversions of alkenes owing to the unproductive transition metal catalysed decomposition of the hydroperoxide.[3] A polybenzimidazole (PBI) supported molybdenum(vi) heterogeneous catalyst (PBI.Mo) has been widely utilised earlier in our laboratory in the epoxidation of alkenes under conditions of excess alkenes[4–8] and therefore further study has now been made to complete the picture of the behaviour of this catalyst and in particular to establish whether good conversion to epoxide is achieved under equimolar conditions.

Epoxidations were performed with cyclohexene **1**, styrene **2**, and 4-vinylcyclohexene **3** (Scheme 1) in small stirred flasks using *tert*-butylhydroperoxide (*t*-BHP) as the oxidant. Reactions were generally performed under N_2 gas to eliminate side-reactions involving O_2 as an oxidant, and each epoxidation was monitored by quantitative gas chromatography. In the case of **3** only the major product, the internal epoxide, was assayed quantitatively. The results using cyclohexene are shown in Table 1, and those for styrene and 4-vinylcyclohexene in Table 2.

Table 1 Epoxidation of cyclohexene using *t*-BHP catalysed by PBI.Mo

Run	PBI.Mo (mmol, mol%)	*t*-BHP[a]/ml, mmol	Cyclohexene/ml, mmol	Toluene/ml	*T*/°C	Epoxide yield[b] (%) (24 h)
1[c]	0.06, 1.2	1.5, 5.2	0.53, 5.2	7.0	80	≈35
2[c]	0.06, 0.3	5.8, 20	2.0, 20	1.2	80	50
3[c]	0.2, 1.0	5.8, 20	2.0, 20	1.2	80	50
4[c]	0.06, 0.3	5.8, 20	2.0, 20	1.2	60	≈25
5[c]	0.2, 1.0	5.8, 20	2.0, 20	1.2	60	≈25
6[d]	0.06, 0.3	5.8, 20	2.0, 20	1.2	60	≈25
7[d]	1.0, 5.0	5.8, 20	2.0, 20	1.2	80	70
8[c,e]	0.06, 1.2	1.5, 5.2	7.5, 73	—	80	100[f] (3 h)
9[d,g]	0.06, 0.4	8.0, 28	1.4, 14	—	80	38
10[c,h]	2.0, 5.0	11.6, 40	4.1, 40	2.3	80	50
11[d,i]	1.0, 5.0	5.8, 20	2.0, 20	1.2	80	65

[a] *t*-BHP in toluene prepared as reported by Sharpless (B. K. Sharpless and T. R. Verhoeven, *Aldrichim. Acta,* 1979, **12**, 63), actual molarity determined by iodometric titration. [b] Based on conversion of cyclohexene. [c] Reaction allowed to equilibrate before *t*-BHP added. [d] All reagents were added before the flask was immersed in an oil-bath and stirring started. [e] Conditions from ref. 5. [f] Based on conversion of *t*-BHP. [g] Cyclohexene:*t*-BHP=1 : 2. [h] Performed in a sealed autoclave system. [i] Reaction performed in air.

Table 2 Epoxidation of styrene and 4-vinylcyclohexene using *t*-BHP catalysed by PBI.Mo

Run	PBI.Mo (mmol, mol%)	*t*-BHP/ml, mmol	Alkene/ml, mmol	Toluene/ml	*T*/°C	Epoxide yield[a] (%) (24 h)
Styrene						
1	Excess styrene reaction from ref. 8					95 (11 h)
2	0.06, 1.2	1.5, 5.2	0.6, 5.2	6.9	80	15
3	1.0, 5.0	5.8, 20	2.3, 20	0.9	85	45
4[b]	2.0, 5.0	11.6, 40	4.6, 40	1.8	80	15
4-Vinylcyclohexene						
5	Excess 4-vinylcyclohexene reaction from ref. 8					87 (33 h)
6	0.06, 1.2	1.5, 5.2	0.7, 5.2	7.3	80	60
7	1.0, 5.0	5.8, 20	2.6, 20	1.1	80	60
8[b]	2.0, 5.0	11.6, 40	5.2, 40	2.2	80	55

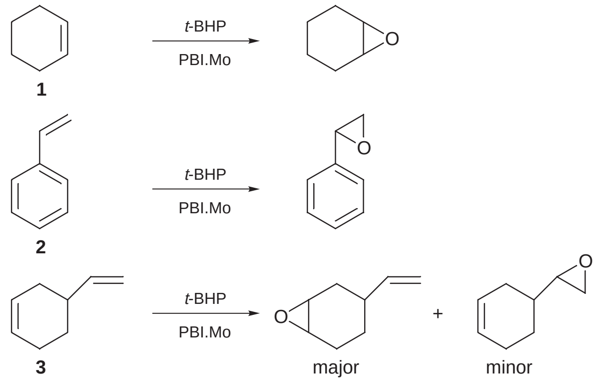
[a] Internal epoxide in the case of 4-vinylcyclohexene. [b] Performed in a sealed autoclave system.

---

*To receive any correspondence (*e-mail*: M.P.A.Smith@strath.ac.uk).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

With cyclohexene a reaction carried out with an excess of alkene and 1.2 mol% Mo (run 8, Table 1), gave a yield of epoxide of *ca.* 100%, based on the consumption of the *t*-BHP. This is in accord with our earlier findings.[4–8] Using the same level of Mo and *t*-BHP but reducing the alkene to an equimolar level (run 1, Table 1) gave a much reduced yield of epoxide, *ca.* 35%, due primarily to the much lower alkene concentration. All subsequent reactions were performed with a considerably reduced volume of toluene, and effectively very much higher concentrations of cyclohexene and *t*-BHP, usually at 1 : 1 molar ratio. The maximum yield of cyclohexene epoxide was *ca.* 70% (run 7, Table 1) achieved by raising the Mo content to 5 mol%. Interestingly, raising the *t*-BHP:cyclohexene ratio to 2 : 1 (run 9, Table 1) did not improve the yield of epoxide relative to that in say runs 2 and 3, where the other conditions are comparable. This is no doubt due to increased *t*-BHP decomposition (see later).



Scheme 1

Some evaporative losses were noticed in reactions performed at 80 °C and to check that this was not limiting the epoxide yields three reactions were carried out at 60 °C (runs 4–6, Table 1). In all cases the epoxide yield dropped significantly. Likewise one reaction was carried out in a sealed autoclave to avoid all material loss (run 10, Table 1) but again the maximum yield of epoxide was disappointing at 50%. Finally with cyclohexene one reaction was performed in a flask open to the air (run 11, Table 1) using the optimum conditions of run 7. While the yield of epoxide was reduced, it was only marginally so.

In nearly all the cyclohexene reactions the GC traces at 24 h showed virtually complete loss of *t*-BHP, most likely indicating that PBI.Mo-catalysed, unproductive decomposition of the hydroperoxide occurs in parallel with the epoxidation reaction. The rate of decomposition of *t*-BHP (14 wt% in xylene at 110 °C) in the presence of 0.02 wt% of Mo-naphthenate has been shown to be fast, with *ca.* 75% decomposition in 2 h.[3] While the loss of *t*-BHP by this mechanism is by no means as fast in the present reactions the limited epoxide yields observed here (maximum 70%) are consistent with the occurrence of a concomitant *t*-BHP decomposition reaction, which seems difficult to suppress without resorting to the use of excess alkene.

The reactions using styrene and 4-vinylcyclohexene were carried out initially under conditions of excess alkene and again good yields of epoxide were obtained [styrene 95% (run 1) 4-vinylcyclohexene 87% (run 5) Table 2].[8] Once again, however, reduction of the *t*-BHP:alkene ratio to 1 : 1 with solvent replacing the alkene deficiency led to lower yields of epoxides (styrene 15%, 4-vinylcyclohexene 60%) (runs 2 and 6, Table 2). Application of the optimum conditions found for cyclohexene led to epoxide yields of 45 and 60%, respectively, for styrene and 4-vinylcyclohexene (runs 3 and 7, Table 2). In the case of 4-vinylcyclohexene the latter yield was no higher than that achieved using low concentrations of alkene and *t*-BHP (runs 7 and 6, Table 2) respectively. Thus overall a very similar pattern of reactivity emerges for these alkenes, with loss of *t*-BHP *via* unproductive, PBI.Mo-catalysed decomposition occurring in parallel with epoxidation.

In conclusion therefore cyclohexene, styrene and 4-vinylcyclohexene can be epoxidised in moderate to good yields using *t*-BHP as the oxidant under equimolar conditions of alkene and *t*-BHP catalysed by PBI.Mo. The latter must be used at a level of at least 5 mol% and inevitably some concomitant catalysed unproductive decomposition of *t*-BHP also occurs. With appropriate choice of conditions, however, it seems that this clean heterogeneous alkene epoxidation catalyst could be useful in commercially interesting small-scale epoxidations.

Experimental

Preparation of PBI-supported Molybdenum(VI) *Catalyst.*—The PBI.Mo catalyst was prepared essentially as reported in our earlier papers.[4,9] The PBI-resin (Hoechst-Celanese Co.) was purified by washing with 0.2 M NaOH for 24 h and deionised water until the washings were neutral, extracted with acetone in a Soxhlet and dried *in vacuo* at 40 °C. Mo was loaded onto the PBI-resin (4.0 g, 22.4 mmol ligand) by refluxing a sample with an excess of $MoO_2(acac)_2$ (8.5 g, 26.0 mmol) (Aldrich) in ethanol for 3.5 h. The beads were allowed to cool, collected by filtration and washed with ethanol before extracting exhaustively (3 days) in a Soxhlet with acetone before drying *in vacuo* at 40 °C. The yield of the PBI.Mo was 5.2 g and the Mo content 2.1 mmol g^{-1} (determined by AAS).

General Procedure for the Epoxidation Reactions.[5]—Alkene, *p*-dichlorobenzene (50% w/v in toluene, 1 ml, GC standard), toluene and PBI.Mo were placed in a 25 ml three-necked round-bottomed flask equipped with an overhead stirrer, a reflux condenser and a septum cap. The mixture was flushed with N_2 and heated at 60 or 80 °C by means of an oil-bath for 20 min to allow equilibration, a toluene solution of *t*-BHP (*ca.* 3.5 M) was added and a sample taken as a commencement of the reaction. The reaction was followed by taking samples at 20 min intervals until 1–2 h, then every hour until 5–6 h and a final sample was taken after *ca.* 24 h when the reaction was finished.

S.-M. L. greatly acknowledges a Research Studentship received from the Neste Oy Foundation, Finland.

Received, 24th May 1999, Accepted, 10th June 1999
Paper E/9/04124I

References

1 M. Braithwaite, in *Chemistry of Waste Minimization,* ed. J. H. Clark, Blackie Academic & Professional, Glasgow, 1995, ch. 2, p. 17.
2 R. Landau, G. A. Sullivan and D. Brown, *CHEMTECH*, 1979, **9**, 602.
3 C. Y. Wu and H. E. Swift, *J. Catal.*, 1976, **43**, 380.
4 M. M. Miller, D. C. Sherrington and S. Simpson, *J. Chem. Soc., Perkin Trans. 2,* 1994, 2091.
5 M. M. Miller and D. C. Sherrington, *J. Catal.*, 1995, **152**, 368.
6 M. M. Miller and D. C. Sherrington, *J. Catal.*, 1995, **152**, 377.
7 G. Ólason and D. C. Sherrington, *React. Funct. Polym.*, 1999, in press.
8 G. Ólason and D. C. Sherrington, *Macromol. Symp.*, 1998, **131**, 127.
9 D. C. Sherrington and S. Simpson, *Reac. Polym.*, 1993, **19**, 13.