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EFFICIENT EPOXIDATION OF TERMINAL AND INTERNAL ALKENES USING *t*-BUTYLHYDROPEROXIDE CATALYSED BY POLYBENZIMIDAZOLE-SUPPORTED Mo(VI).(PBI.Mo)

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Abstract: A polybenzimidazole-supported Mo complex (PBI.Mo) has been prepared by a method already reported. Extensive investigation of digestion procedures has shown a dry-ashing method using $NaNO_3/HNO_3$ (conc.) at 560°C to be an optimal method for preparing samples for Mo analysis by atomic absorption spectrophotometric methodology. Mo loadings in the range 1.32-0.62 mmol Mo g^{-1} polymer were demonstrated. PBI.Mo has been used as a heterogeneous catalyst in the epoxidation of cyclohexene, methylene-cyclohexane, 4-vinyl cyclohexene, styrene, 1,3-pentadiene and allyl chloride, bromide and alcohol using *t*-butylhydroperoxide as the oxidant. The catalyst is very effective for the first four substrates, somewhat less active than soluble MoO_2acac_2, but providing final yields and purity of products generally better than using MoO_2acac_2. The 1,3-pentadiene displays an overall conversion of ~35% with a distribution of the four possible monoepoxide isomers similar to that obtained with MoO_2acac_2 as catalyst. The allylic substrates showed poor conversion probably as a result of secondary (oligomerisation) reactions involving the epoxide products. Running the epoxidations for extended periods in air allows *in situ* generation of alkyl hydroperoxides in the case of cyclohexene and 4-vinylcyclohexene and these are then effective internal oxidants for further Mo catalysed epoxidation of these alkenes. When run under anaerobic conditions the reactions are very clean with no evidence of any free radical processes contributing. In all cases Mo leaching is minimal. Good activity is seen in the recycling of PBI.Mo in the case of styrene and 1,3-

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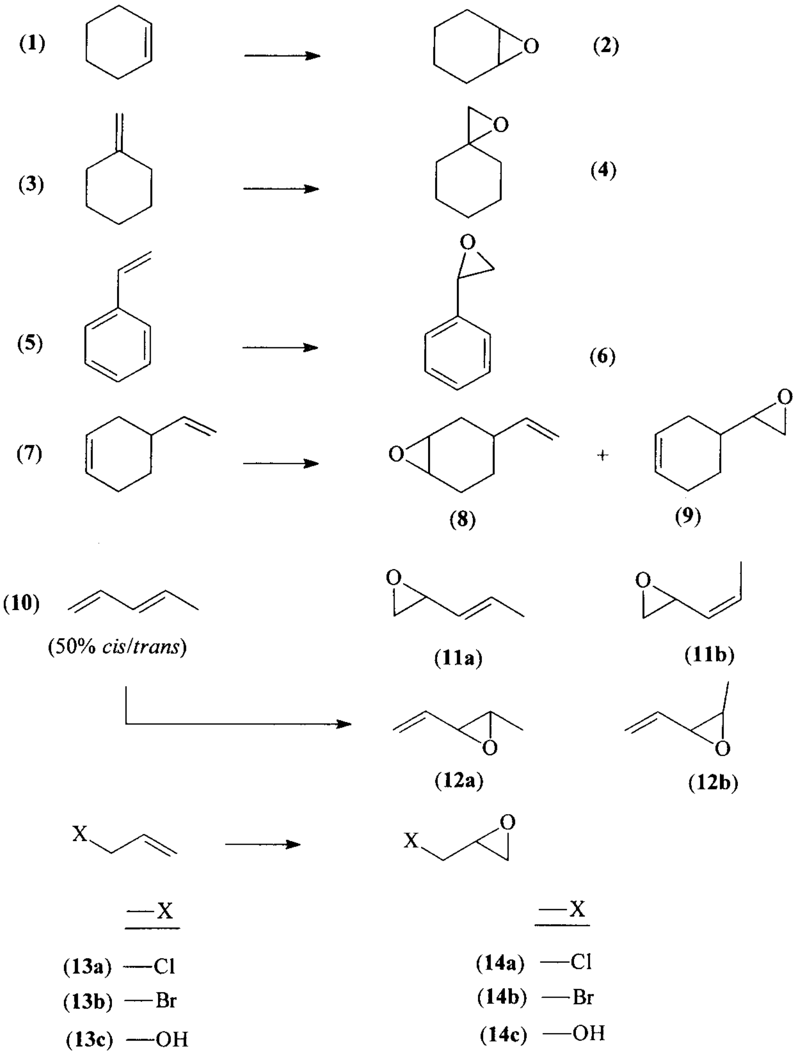


Scheme 1 Epoxidation of Alkenes by *t*BHP Catalysed by Homogeneous MoO_2acac_2 and Heterogeneous PBI.Mo.

pentadiene, although with cyclohexene and 4-vinylcyclohexene steady deactivation is seen, probably as a result of catalyst fouling. Thermogravimetric analyses suggest that it might be possible to burn off the foulant without destroying the catalyst.

INTRODUCTION

The use of macromolecular metal complexes as oxidation catalysts was reviewed in 1988 (Ref.1) and since then the area has continued to thrive. Recent contributions have been made by the groups of Tempesti (Ref. 2); Jiang (Ref. 3); Maslinska-Solich (Ref. 4); Lindsay-Smith (Ref. 5); Kumar (Ref. 6); and Hassanein (Ref. 7). The above have focussed on oxidation reactions with relevance to the commodity or bulk chemicals markets, but there has also been increasing activity in the immobilisation of asymmetric metal complex oxidation catalysts (Refs. 8-11) for potential application in the field of specialities and intermediates. As far as are own work on bulk chemicals is concerned we have focussed on the epoxidation of cyclohexene (Ref. 12) and propene (Ref. 13) using *tert*-butylhydroperoxide (*t*BHP) as the oxidant with Mo(VI) immobilised on a thermo-oxidatively polybenzimidazole resin (PBI) as the heterogeneous catalyst. We have argued that a realistic possibility for technological application (as opposed to laboratory use) of polymer catalysts in oxidation reactions is most likely to arise only with polymer supports with significant and prolonged chemical stability in an oxidising environment. We now report our results on the use of PBI.Mo in the epoxidation of a wider range of alkenes (Scheme 1) each of potential technological importance. In the case of terminal alkenes, interest centres on the fact that the product epoxides are particularly sensitive to further reaction (Ref. 14).

EXPERIMENTAL

Materials

PBI, MoO_2acac_2, *t*BHP, toluene and bromobenzene were supplied and prepared for use as previously reported (Ref. 13). Cyclohexene (**1**), cyclohexene oxide (**2**), methylene cyclohexane (**3**), styrene (**5**), styrene oxide (**6**), allyl chloride (**13a**), bromide (**13b**) and alcohol (**13c**) epichloro (**14**) and epibromohydrin (**14b**) and glycidol (**14c**) were supplied by

Aldrich. 4-Vinylcyclohexene (7) and 4-vinylcyclohexene dioxide were supplied by Fluka. 1,3-Pentadiene (**10**) (50% *cis*/*trans* mixture) was made up from a 92% *cis* grade and a 79% *trans* grade, both supplied by B.P. Chemicals. Vinyl acetate was from B.D.H. 1-Oxaspiro[2,5]octane (**4**) was synthesised in house from cyclohexanone (B.D.H.) using a sulfur ylide method developed by ICI (Ref. 15). 2-(Cyclohex-3-enyl)oxirane (**9**) was synthesised similarly from 1,2,3,6-tetrahydrobenzaldehyde (Aldrich). 4-Vinylcyclohex-1-ene 1,2-epoxide (**8**) was prepared from 4-vinylcyclohex-1-ene by epoxidation using *t*BHP in the presence of our own catalyst, PBI.Mo, followed by appropriate purification. The four monoepoxides (**11a,b; 12a,b**) of 1,3-pentadiene (50/50:*cis*/*trans*) were prepared using *m*-chloroperbenzoic acid in the usual way, and separation and purification was achieved with a 1.5 metre spinning band distillation unit. *t*-Butylcyclohex-2-enyl peroxide (**16**) was prepared by reaction of *t*BHP with cyclohexene at 70°C for 5 days in the presence of Cu(II) as catalyst. (**16**) was purified by vacuum microdistillation. All synthesised compounds yielded acceptable elemental microanalytical data and ^{1}H NMR spectra.

Mo standards were from B.D.H. and KNO_3, $NaNO_3$ and Na_2O_2 from Fisons. cH_2SO_4 and $cHNO_3$ were reagent grade acids and H_2O_2 (30% aq) was from B.D.H.

Catalyst Preparation and Analysis

The polybenzimidazole-supported Mo complex (PBI.Mo) was prepared as reported earlier (Ref. 13). Three different batches were examined in this work with different Mo loadings: PBI.Mo.I (1.32 mmole Mo g^{-1}); PBI.Mo.II (1.16 mmole Mo g^{-1}) and PBI.MoIII (0.62 mmol Mo g^{-1}). Previous samples of PBI.Mo have been assayed for Mo by digestion in *aqua regia* (wet-ashing) followed by dilution and analysis by standard atomic absorption spectrophotometric (AAS) methodology. For reasons which are not entirely clear the present samples proved somewhat resistant to this approach and so a number of "dry-ashing" methods were also examined as follows.

Typically a ground sample of PBI.Mo (0.04 g) was weighed into a silica or graphite crucible with $NaNO_3$ or KNO_3 (0.5 g). This mixture was wetted with $cHNO_3$ (2 ml) and then placed into a cold muffle furnace. The furnace temperature was raised to 110°C for 30 minutes, then ramped to 560°C at a rate of 2°C min^{-1}. The temperature of 560°C was maintained for one hour before the crucible was removed and allowed to cool to room temperature. Water (20 ml) was added and the solution left overnight. It was then transferred quantitatively to a volumetric flask (100 ml) and nitric acid (10 ml) added before making up to the mark with deionised water.

When a nickel crucible was used with $NaOH/Na_2O_2$ the crucible was first heated to 450°C with NaOH (0.5 g). After cooling to room temperature Na_2O_2 (0.5 g) was added along with ground PBI.Mo (~0.04 g). Heating was resumed with the furnace ramped slowly to 370°C. After 2 hours the crucible was removed, somewhat cooled, and a second sample of Na_2O_2 added. The peroxide was then ignited on a Bunsen burner. The crucible was allowed to cool, was filled with deionised water and the solution prepared for AAS analysis as before.

The results of the analyses are summarised in Table 1 in the case of PBI.Mo.I and PBI.Mo.II. PBI.Mo.III was analysed by dry-ashing with $NaNO_3/HNO_3$ to yield an Mo content of 0.62 mmole Mo g^{-1}.

Epoxidation Reactions

These were carried out essentially as reported before (Ref. 13). Typically alkene (7.5 ml, ~58-133 mmole), bromobenzene (0.5 ml) as an internal standard for GC analysis, toluene (~0.5 ml to bring total volume to 10 ml) and PBI.Mo (mass equiv. to 0.038-0.10 mmole Mo) were placed in a small jacketed round-bottomed flask fitted with a reflux condenser, an overhead mechanical stirrer and a septum sampling arm. A thermo-regulated circulation bath was used to bring the reaction vessel usually to 60°C, then the toluene solution of *t*BHP (typically ~1.5 ml/3.5M ≡ 5 mmole) was injected in to start the reaction. Samples were withdrawn at regular intervals and the products quantified by GC using routine standardisation and evaluation procedures.

For comparison all epoxidations were also performed under similar conditions using soluble MoO_2acac_2 as the catalyst.

Typical conversion/time curves for reactions employing cyclohexene, methylenecyclohexane, styrene, 4-vinylcyclohexene and *cis*/*trans* 1,3-pentadiene are shown in Figures 1-5 respectively where conversion (%) is calculated on the basis of *t*BHP consumed (i.e. 5 mmole ≡ 100% product) since (on safety grounds) the alkene is present in excess. The numerical data

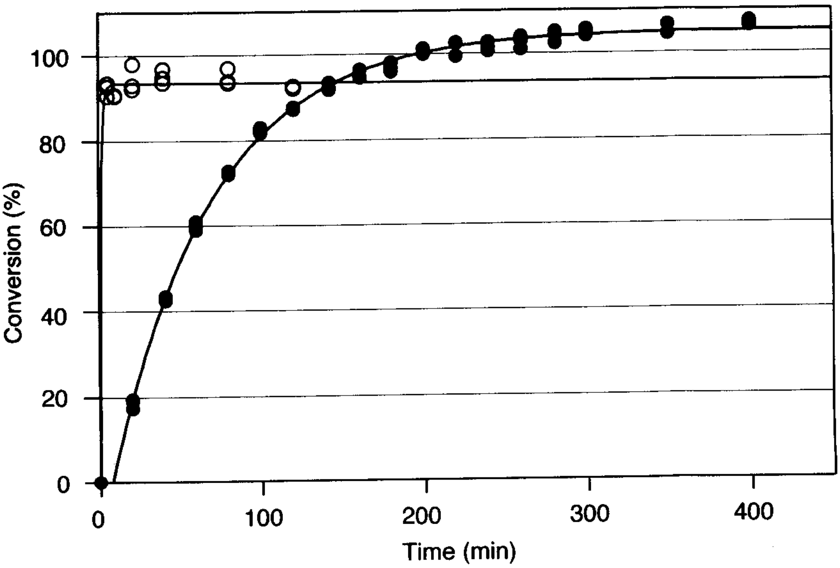


Figure 1 Epoxidation of Cyclohexene with *t*BHP Catalysed by: ○, MoO_2acac_2; ● PBI.Mo.II.

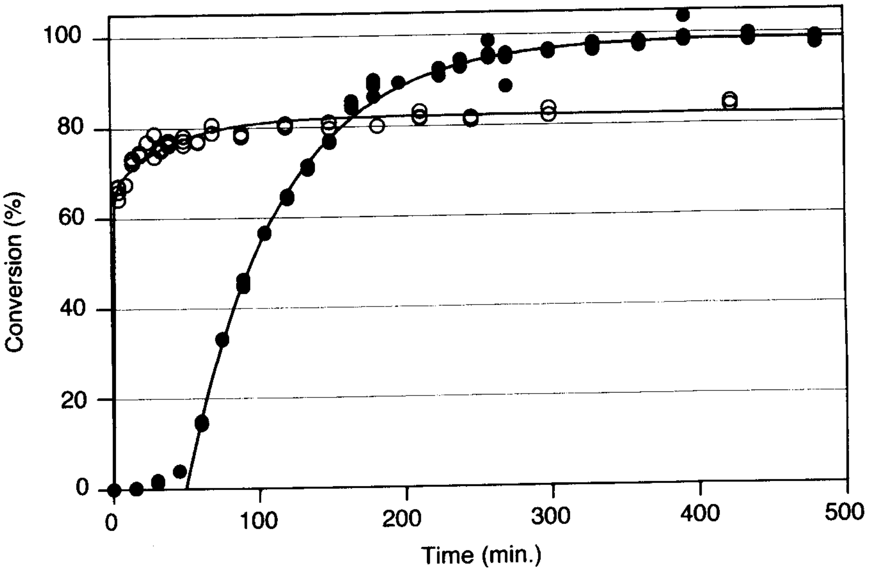


Figure 2 Epoxidation of Methylene Cyclohexane with *t*BHP Catalysed by: ○, MoO_2acac_2; ● PBI.Mo.II.

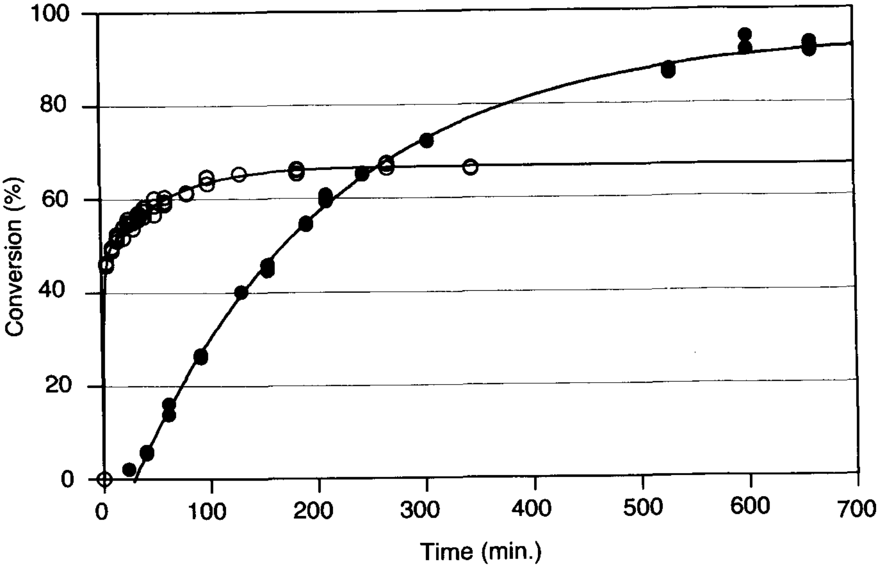


Figure 3 Epoxidation of Styrene with *t*BHP Catalysed by: ○, MoO_2acac_2; ● PBI.Mo.II.

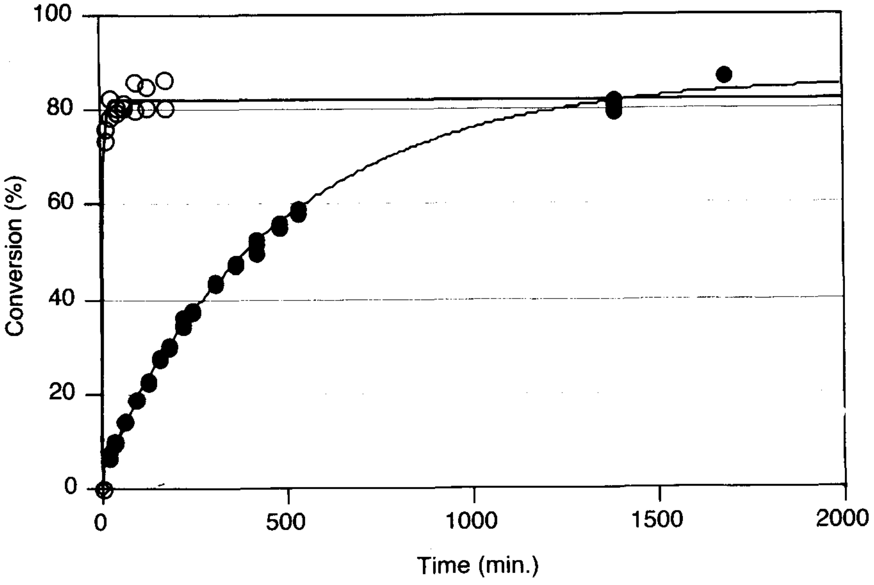


Figure 4 Epoxidation of 4-Vinylcyclohexene with *t*BHP Catalysed by: ○, MoO_2acac_2; ● PBI.Mo.II.

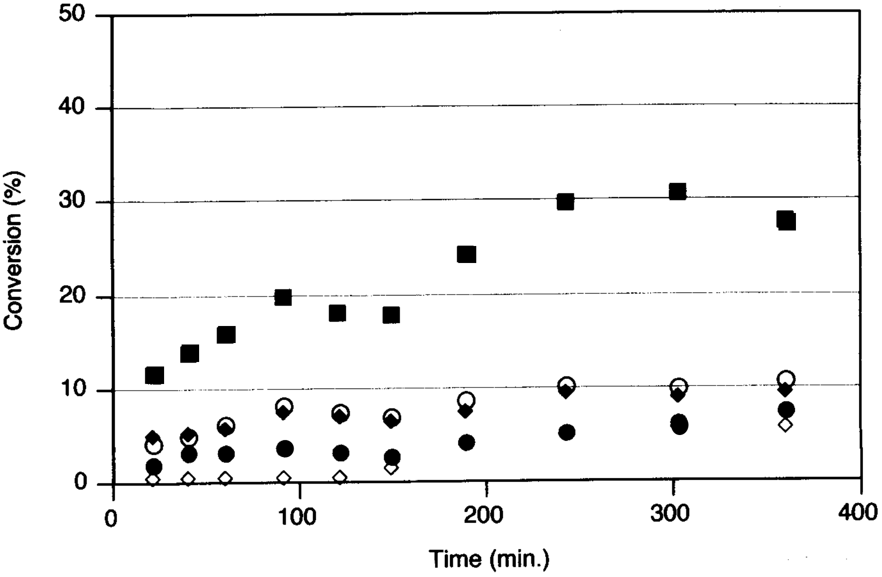


Figure 5 Epoxidation of 1,3 Pentadiene with *t*BHP Catalysed by PBI.Mo.II: ◇ (**11a**); ● , (**11b**); ◆, (**12a**); ○, (**12**); ■ total epoxides.

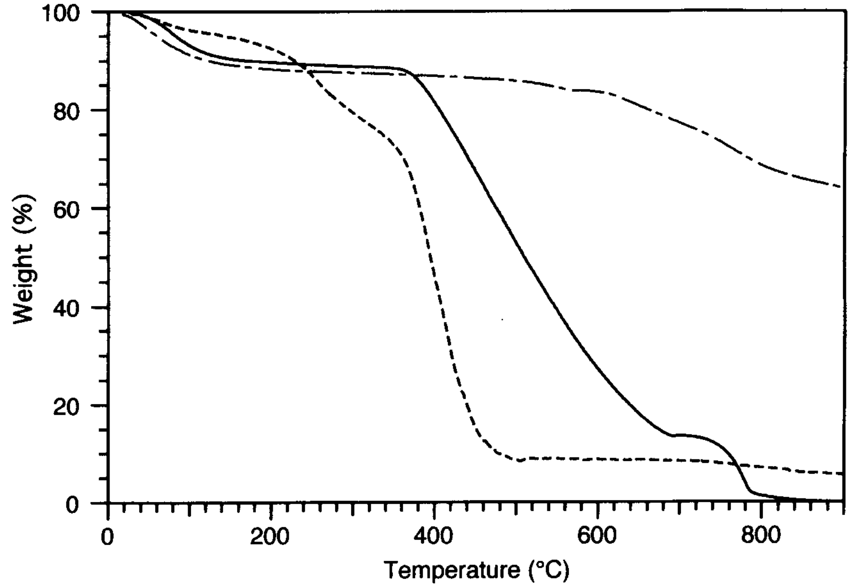


Figure 6 TGA Traces for: — - —; PBI; —— PBI.Mo.II; - - - - PBI.Mo.II (used).

Table 1 Mo Loading of PBI.Mo determined via AAS Following Different Digestion Procedures

Digestion Medium	Wet (W) or Dry (D)	Conditions	PBI.Mo.I (mmol Mo g^{-1})	PBI.Mo.II (mmol Mo g^{-1})
aqua regia[a)]	W	glass tube, room temp.	0.97	0.60
aqua regia	W	glass tube, ultrasonic bath	NP[b)]	0.69
aqua regia	W	glass tube, hot plate	1.15	0.77
aqua regia	W	glass tube, hot air gun	1.30	0.97
CH_2SO_4/$cHNO_3$ (1:1)	W	glass tube, room temp.	0.34	NP
CH_2SO_4/$cHNO_3$ (1:1)	W	glass tube, ultrasonic bath	NP	0.33
cH_2SO_4/H_2O_2	W	glass tube, room temp.	0.26	NP
$NaNO_3$/$cHNO_3$	D	dense graphite crucible 420°C	0.51	0.49
$NaNO_3$/$cHNO_3$	D	nuclear grade graphite crucible 420°C	0.55	0.54
$NaNO_3$	D	silica crucible 560°C	1.13	0.67
KNO_3/$cHNO_3$	D	silica crucible 560°C	1.13	0.88
$NaNO_3$/$cHNO_3$	D	silica crucible 560°C	1.32	1.16
Na_2O_2/NaOH	D	nickel crucible 450°C	1.15	0.88

a) cHCl/$cHNO_3$ (3:1 v/v); b) NP = not performed

obtained are summarised in Tables 2 and 3 for the heterogeneous PBI.Mo and soluble MoO_2acac_2 catalysts respectively, with the turnover frequency (TOF, mmol prod. mmol Mo^{-1} min^{-1}) usually being calculated at the time for 50% conversion.

TOF data is not intended to represent a rigorous kinetic parameter, but are offered to provide a convenient and simple comparison of reaction rates under the conditions employed.

RESULTS AND DISCUSSION

Catalyst Preparation and Analysis

The preparation of PBI.Mo was as reported before and some batch to batch variation in the level of Mo immobilised was detected. In addition it was found that our earlier digestion procedure prior to Mo assay by AAS utilising *aqua regia* was not always satisfactory and so we have explored a range of other wet and dry ashing methodologies. The results are

Table 2 Epoxidation of Alkenes by *t*-Butylhydroperoxide Catalysed by PBI.Mo.II[a]

alkene (mmol)	PBI.Mo.II (mmol Mo)	Temp. (°C)	Product	Max. Con. (%) Time (min)	TOF[b] (mol prod. mol Mo^{-1} min^{-1})
cyclohexene (74)	0.038	60	**(2)**	105(400)	1.36
methylenecyclohexane (63)	0.038	60	**(4)**	99(400)	0.70
styrene (65)	0.038	60	**(6)**	95(700)	0.38
4-vinylcyclohexene (58)	0.038	60	**(8)** **(9)** dioxide	87(2000) 15(2000) ~ 0	0.41 0.17 ~ 0
1,3-pentadienes (75) (50% *cis*/*trans*)	0.038	60	**(11a)** **(11b)** **(12a)** **(12b)**	~ 6(300) ~ 8(300) 10(300) 11(300)	~ 0.03 0.10 0.21 0.24
allyl chloride (92)	0.10	45	**(14a)**	30(400)	0.06[c]
allyl bromide (86)	0.10	45	**(14b)**	~ 6(400)	< 0.01[c]
allyl alcohol (133)	0.10	45	**(14c)**	~ 5(400)	< 0.01[c]

a) See experimental for other conditions; b) at time of ~50% conversion; c) at time of 20% maximum conversion.

summarised in Table 1 from which we conclude that the most effective method in our hands is to dry ash with $NaNO_3/cHNO_3$ at 560°C in a silica crucible. This yields our highest values for the Mo content of PBI.Mo.I and PBI.Mo.II of 1.32 and 1.16 mmol Mo g^{-1} respectively, and since we believe that we are unlikely to see any artefacts leading to an overestimate of the Mo loading, we conclude that these maximum data are the best estimate of the real Mo contents. In sample PBI.Mo.III, where we suspected a rather low incorporation of Mo, the $NaNO_3/cHNO_3$ dry ashing technique yielded a value of 0.62 mmole Mo g^{-1} resin. Rather interestingly thermogravimetric analytical traces (Figure 6) for PBI and PBI.Mo.I-III showed the virgin polymer to be stable in O_2 to well above 600°C whereas the Mo loaded species showed rapid degradation ensuing above ~400°C with the generation of a residue stable up to

Table 3 Epoxidation of Alkenes by *t*-Butylhydroperoxide Catalysed by Soluble MoO_2acac_2 [a)]

alkene (mmol)	MoO_2acac_2 (mmol x 10^2)	Temp. (°C)	Product	Max.Con (%) Time(min)	TOF (Mol prod. mol $Mo^{-1}min^{-1}$)	TOF_{homo}/TOF_{hetero}
cyclohexene (74)	0.12	60	**(2)**	93(20)	36	26.4
methylene cyclohexane (62)	0.12	60	**(4)**	82(150)	15	21.4
styrene (65)	0.13	60	**(6)**	66(200)	3.5	9.2
4-vinylcyclo-hexane (58)	0.13	60	**(8)**	83(100)	3.0	7.3
			(9)	15(100)	0.32	1.8
			dioxide	~ 0	~ 0	~ 1
pentadienes (75) (50% *cis*/*trans*)	0.19	60	**(11a)**	7(100)	~ 0.13	~ 4.3
			(11b)	4(100)	0.33	3.3
			(12a)	17(100)	0.52	2.5
			(12b)	17(100)	0.64	2.7
allyl chloride (92)	0.12	45	**(14a)**	65(250)	0.60[b)]	10
allyl bromide allyl alcohol	0.12	45	complex reaction products			

a) See experimental for other conditions; b) at time of ~40% maximum conversion

~700°C as we have reported before (Ref. 13). If the residue is assumed to be MoO_3 and there are no losses via volatilisation of this, back calculation indicates that the loadings of PBI.MoI-III to be 0.93, 0.87 and 0.74 mmol Mo g^{-1} respectively. While the correlation with AAS data is not good, the trends are similar and this relatively inaccurate method yields data at least of the correct order of magnitude. In the case of PBI and PBI.Mo.I-III there is a significant mass loss between ~20-350°C amounting in some cases to ~20%. Brooks *et al* (Ref. 16) have independently reported water contents of ~15% in PBI and in our hands we can recover ~5% water by vacuum drying in a pistol at 150°C for 48 hours. The losses seen in TGA may therefore include some sorbed organics. In the case of a sample of PBI.Mo.II which had been used in the epoxidation of 4-vinylcyclohexene over an extended period (24 hours) and without exclusion of O_2 (see later), TGA analysis shows a major reduction in mass loss over the temperature range 0-150°C (no H_2O present?) but a significant shoulder on the mass loss curve ~225-375°C. In isolating and recovering this catalyst sample after use in catalysis and before TGA analysis a noticeable oligomeric organic contaminant (fouling) was observed and we believe this mass loss corresponds to the degradation of this contaminant. This suggests that PBI.Metal catalysts maybe regenerable in terms of burning-off organic contaminants which foul the catalyst providing the burn-off is controlled within the ~200-300°C temperature window. This possibility needs to be investigated further.

Catalysed Epoxidations

Examination of the data in Tables 2 and 3 shows that the PBI.Mo. heterogeneous species is an active and selective catalyst for the epoxidation of external alkenes such as styrene and methylenecyclohexane. In general the activity is well below that of soluble MoO_2acac_2 (TOF_{homo}/TOF_{hetero} typically ~10-20) but nevertheless the level of activity is high enough to be of synthetic utility. The poorer kinetic performance may simply arise from diffusional limitations in the polymer-supported species. To some extent the lower activity is off-set by the higher selectivity displayed by PBI.Mo. relative to MoO_2acac_2. This is reflected in the higher ultimate yields achieved, for example, for production of cyclohexene oxide, 1-oxaspiro[2,5]octane, styrene oxide and 4-vinylcyclohexene-1,2-epoxide. The ability to produce highly reactive epoxides such as styrene oxide and 1-oxaspiro[2,5]octane in high yield without contamination from subsequent products arising from Lewis acid ring-opening of these epoxides is also very rewarding (Ref. 14) and perhaps worthy of further investigation in say natural product syntheses. The yield of 105% for cyclohexene oxide is real, and is explained in terms of a contribution from O_2 as an oxidant (see later).

As perhaps expected the major regio-isomeric product in epoxidation of 4-vinylcyclohexene is the internal product 4-vinylcyclohexene-1,2-epoxide, (**8**). The corresponding terminal epoxide, 2-(cyclohex-3-enyl)oxirane, (**9**) was formed in much lower yield and the selectivity was about the same with the PBI.Mo catalyst as with MoO_2acac_2. No diepoxide product was detected under the conditions employed.

The results of epoxidations of 1,3-pentadiene (50% *cis/trans*) using PBI.Mo parallel the results from MoO_2acac_2 as a catalyst. All four possible epoxide products ((**11a,b**) and (**12a,b**)) are formed in a roughly similar ratio with both the heterogeneous and homogeneous catalysts. Under the experimental conditions used i.e. excess alkene or limited oxidant, no bisepoxide products were observed.

The potentially interesting epoxidations of allyl chloride, bromide and alcohol proved disappointing. Epichlorohydrin was formed in modest yield with MoO_2acac_2 (~65%) which dropped to ~30% with the supported catalyst. For the bromide and alcohol the polymer catalyst was extremely poor, although it gave somewhat cleaner reactions than MoO_2acac_2. Overall the problem with these substrates appears to be the very high reactivity of the product epoxides. Almost certainly the epoxidation reactions proceed quite well but secondary reactions of the epoxides occur leading to oligomeric products. Attempts to epoxidise vinyl acetate yielded reaction mixtures from which only acetic acid could be clearly identified.

Recycling Experiments

In order to assess the prospects for using PBI.Mo continuously some simple recycling experiments were performed. These catalysed reactions were run under normal conditions but for an extended period of time (24 hours). At the end of the first reaction the product mixture was decanted from the polymer catalyst, the latter was washed with solvent and then a second batch of substrate, oxidant etc introduced. The results obtained are summarised in Table 4.

In agreement with our earlier observations (Ref. 12) PBI.Mo deactivates rapidly in the case of cyclohexene as the substrate with the same pattern being repeated with 4-vinylcylohexene. In complete contrast PBI.Mo becomes increasingly active when recycled with styrene or 1,3-pentadiene as the substrate. We have recorded this substrate dependent recycling behaviour before (Ref. 13) in the case of propene, when re-use or ageing of the catalyst gives rise to remarkably enhanced activity and maintained high selectivity. In the case of cyclohexene and 4-vinylcyclohexene it seems most likely that secondary reactions involving the substrate and/or the products foul the polymer support whereas this does not occur with styrene and 1,3-pentadiene. The enhanced activity on recycling might arise from morphological changes in the polymer allowing access to a greater number of catalytic sites.

Effect of O_2, 3,5-di-t-butyl Catechol and N_2

The first entry in Table 2 indicates with PBI.Mo catalyst a yield of cyclohexene oxide of 105% based on the oxidant *t*BHP. Further experiments proved that this was a real result. These epoxidations were carried out as normal but for an extended period of time (24 hours) and then they were repeated either with added 3,5-di-t-butyl catechol (0.2 g), or with an N_2 atmosphere. The results are summarised in Table 4. For cyclohexene these show that the yields of epoxide, 2-cyclohexen-1-ol and 2-cyclohexen-2-one are respectively 168, 94 and 23% based on the 5 mmol of tBHP oxidant. Clearly molecular O_2 is intervening as an oxidant in these reactions. This was confirmed by addition of a radical scavenging agent 3,5-di-*t*-butyl catechol, and ultimately by displacement of air from reaction mixtures with N_2. Under a N_2 atmosphere the conversion of cyclohexene to its oxide was ~100% based on the added *t*-BHP and there were no allylic oxidation products detected. Interestingly recycling of the catalyst showed its activity to have fallen (100 → 76% epoxide) and so this deactivation is not related solely to an O_2 induced free radical process.

Parallel behaviour was displayed by 4-vinylcyclohexene where addition of the radical scavenger or better utilisation of a N_2 atmosphere eliminated all free radical allylic oxidation products. In this instance PBI.Mo maintained its activity over two runs, but more data is needed to confirm this stability. O_2 induced free radically derived products proved not to be a problem in epoxidations of styrene and 1,3-pentadiene.

The yield of 168% cyclohexene oxide, entry 1, Table 4, is a most interesting one and suggests that autoxidation of cyclohexene to cyclohex-2-enyl hydroperoxide (**15**) generates the latter *in situ* (Scheme 2). This species could then function as the oxidant with PBI.Mo catalyst, fragmenting heterolytically in the epoxidation of more cyclohexene, generating yields of the

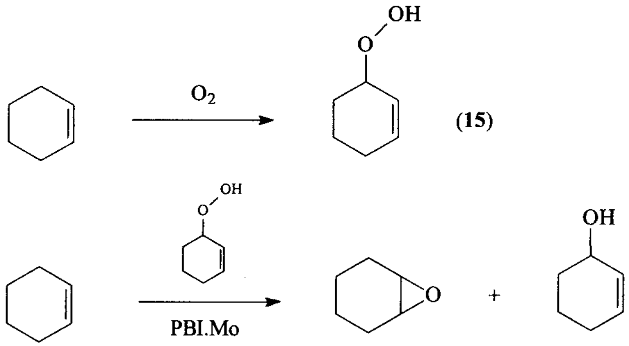
Table 4 Recycling of PBI.Mo.II Catalyst and Effect of added 3,5-Di-*t*-butyl Catechol and N_2 atmospherea)

Alkene/ Conditions	Run	Epoxide (%)	Other Products (%)	
cyclohexene		**(1)**	2-cyclohexen-1-ol	2-cyclohexen-1-one
air	1	168	94	23
	2	94	114	48
	3	6	7	11
catechol	1	43	0	0
N_2	1	102	0	0
	2	76	0.5	0
styrene		**(6)**		
air	1	91	0c)	0c)
	2	103	0c)	0c)
	3	112	0c)	0c)
4-vinylcyclo-hexene		**(8)**	**(9)**	allylic oxidation
air	1	63	5	b)
	2	22	4	b)
	3	14	5	b)
catechol	1	37	0	0
N_2	1	61	0	0
	2	62	0	0
1,3-pentadiene		all monoepoxidesd)		
air	1	21		
	2	56		
	3	53		

a) 60°C for 24 hours, see text for recycling details; b) complex and not quantified; c) no other products seen; d) total yield sum of all epoxides

latter in excess of 100% (based on the original *t*BHP feed) and 2-cyclohexen-1-ol as the allylic oxidation by-product. Further oxidation of the latter to 2-cyclohexene-1-one is readily envisaged, and indeed this species is also detected as a product in aerobic reactions (Table 4).

The possibility exists therefore of developing a PBI.Mo-based heterogeneous process without a feed of alkylhydroperoxide, but rather generating the latter *in situ* from O_2. In a formal sense therefore the epoxide product would be formed from O_2.

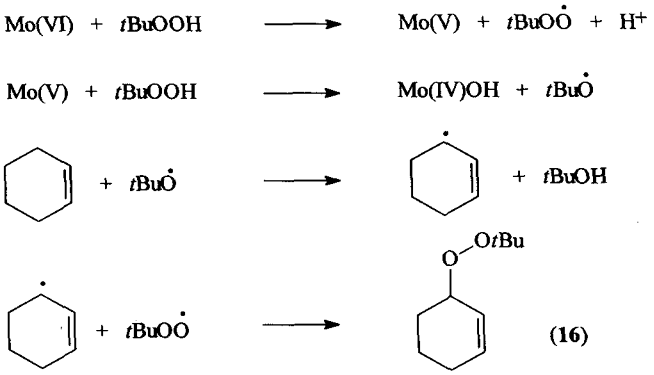


(15)

Scheme 2 *In-situ* formation of Cyclohex-2-enyl Hydroperoxide as the Oxidant for PBI.Mo Catalysed Epoxidation of Cyclohexene

Additional Free Radical Processes

Further confirmation of the contribution of free radical processes arose in the case of catalyst PBI.Mo.III. This has a significantly lower loading of Mo (0.62 mmol Mo g^{-1}) than batches I and II and consequently a much higher level of benzimidazole groups not co-ordinated to Mo centres. When used as a catalyst in the epoxidation of cyclohexene (74 mmol cyclohexene; 0.18 mmole Mo; 5 mmole tBHP; 80°C) a maximum yield of epoxide of ~45% (150 min) was achieved (Figure 7) significantly lower than with the more highly loaded catalysts. Very significantly *t*-butylcyclohex-2-enyl peroxide (**16**) was detected in significant quantities in the reaction mixture. Sheldon and Kochi (Ref. 17) have postulated a competing free radical process with Mo-based catalysts which is driven by the sorption of H^+ (Scheme 3). The free imidazole groups in PBI.Mo.III could readily act as protonation sites (or proton abstractors) favouring the initial reaction in Scheme 3. The subsequent free radical processes generating (**16**) could then follow quite logically. Consumption of *t*BHP in these processes would of course limit its availability for heterolytic fission and epoxide formation.



(16)

Scheme3 Mo Catalysed Free Radical Decomposition of *t*BHP and Formation of *t*-Butyl Cyclohex-2-enyl Peroxide from Cyclohexene

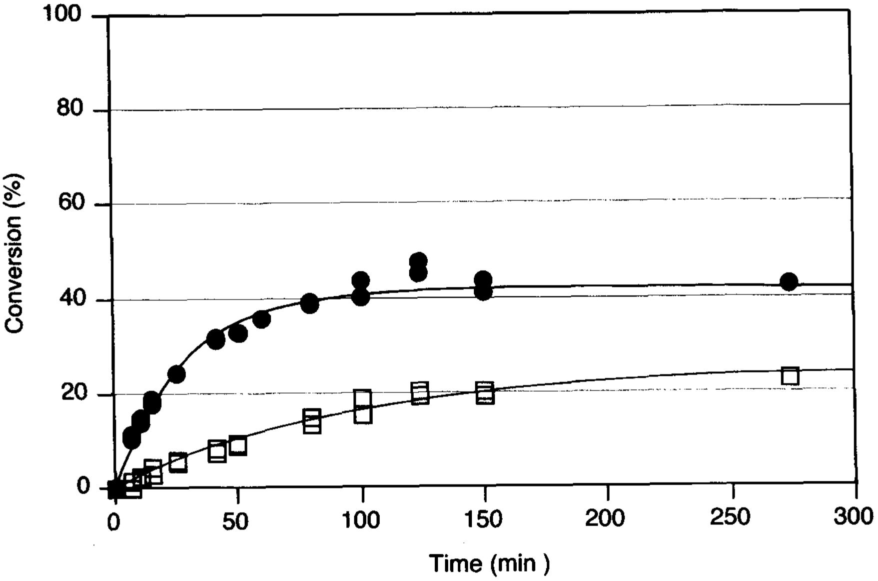


Figure 7 Epoxidation of Cyclohexene with *t*BHP Catalysed by PBI.Mo.III; ● epoxide; ☐ , *t*-butylcyclohexenyl peroxide.

Catalyst Leaching

We have previously reported in detail on the leaching of Mo(VI) from PBI.Mo during extensive recycling of this catalyst (Ref. 12, 13) and certainly in the case of propene and cyclohexene as the substrate the levels are very low. Indeed, in the case of propene the potential long-term stability and use of the catalyst look very promising. Table 5 summarises the results of monitoring the levels of Mo in the supernatant solutions from standard catalytic epoxidations of various alkenes using digestion and AAS methods.

The initial levels of leaching of Mo, irrespective of alkene substrate and conditions (aerobic, anaerobic or with radical scavenger) are low, indeed, somewhat lower than we have previously reported (Ref. 12, 13). This may simply reflect the rather lower loadings of Mo on PBI.Mo.I-III (1.32, 1.16 and 0.62 mmol Mo g^{-1}) and the lower leaching values may correspond simply to rather lower levels of a physically trapped and more easily leached component of Mo complex in the support. The present data also refers to reactions run for a longer period (24 hours) than previously (1-4 hours) and so the lower leaching initial levels are even more surprising. In the case of cyclohexene and 4-vinylcyclohex-ene as substrates recycled catalyst seems to show lower levels of leaching indeed, falling below our detection

Table 5 Mo Leaching Data from PBI.Mo Catalysed Epoxidations of Various Alkenes[a)]

Mo leached (%)[b)]								
Alkene	Cyclohexene			4-Vinylcyclohexene			Styrene	1,3-Penta diene
Run	Air	Catechol	N$_2$	Air	Catechol	N$_2$	Catechol	Air
1	0.27	0.65[c)]	~0[c)]	0.01	1.16[c)]	0.42[c)]	0.54	0.43
2	0.48	N.P.[d)]	~0[c)]	~0	N.P.	N.P.	1.20	0.41
3	~0	N.P.	N.P.	~0	N.P.	N.P.	0.59	0.33

a) See Table 2 and Text for Reaction Conditions; b) Data = % Mo originally on PBI.Mo found in supernatant solution; Detection limit ~0.01%; c) PBI.Mo.III, otherwise PBI.Mo.I; d) N.P. = not performed.

limit and again this confirms our earlier findings. Rather surprisingly, however, the initial low levels of leaching seen with styrene and 1,3-pentadiene as substrates seem to be maintained on reuse of the catalyst. Why this difference arises is by no means clear and further investigations are needed to confirm and explain these results. Overall, however, PBI.Mo shows rather high stability with oxidation of all the alkenes studied.

CONCLUSIONS

PBI.Mo in combination with *t*BHP is a powerful epoxidation catalyst for a number of alkenes generating epoxides cleanly and in high yield. This is so even in the case of reactive epoxides such as styrene oxide and 1-oxaspiro[2,5]octane. Under aerobic conditions allylic oxidation products can also be formed. The catalyst is readily recyclable and shows relatively low Mo leaching characteristics. Catalyst activity remains high with e.g. styrene, but falls progressively on re-use with e.g. 4-vinylcyclohexene. Catalyst fouling is the most likely cause. TGA analyses suggest that the foulant may be removable by heating in O_2 to ~300°C, while leaving the catalyst in tact.

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