A High Activity Molybdenum containing Epoxidation Catalyst and its Use in Regioselective Epoxidation of Polybutadiene

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MoO_2Cl_2[3-(diethoxyphosphinyl)camphor] is a highly active catalyst for the epoxidation of alkenes by Bu^{t}OOH; for polybutadiene containing *cis*-1,4-,*trans*-1,4-, and 1,2-polymerised units, very high selectivity to the backbone double bonds is observed.

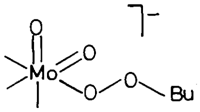
It is now generally accepted[1] that the active species in epoxidations of alkenes by *e.g.* Bu^{t}OOH catalysed by dioxomolybdenum(VI) complexes contains the Bu^{t}OOH co-ordinated to the metal *via* one of its oxygen atoms in a distorted octahedral complex (**1**). Since most suitable catalyst precursors are themselves octahedral, it is necessary for a ligand to dissociate to create a vacant site for co-ordination of the Bu^{t}OOH. A possible strategy to obtaining high activity for such catalysts would be to employ a bidentate ligand in which one of the donor atoms is only weakly bound to the molybdenum centre so that it stabilises the catalyst precursor but readily deco-ordinates to allow co-ordination of the Bu^{t}OOH.

We have recently prepared[2] the β-ketophosphonate complex of Mo^{VI}, (**2**), in which the Mo–O bond lengths suggest significantly stronger binding of the phosphoryl oxygen atom than of the carbonyl. The lability of the carbonyl oxygen atom is clearly shown by the reaction with more of the β-ketophosphonate ligand to give (**3**), in which the two organic ligands are bound in a monodentate fashion through the phosphoryl oxygen atom.[2] We now report the use of these complexes for alkene epoxidation.

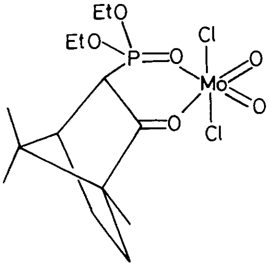
Table 1 shows that (**2**) catalyses the epoxidation of a wide range of alkenes giving high yields of product with very little side reaction, although it is not active for styrene epoxidation.

Figure 1 shows kinetic studies on the epoxidation of 1-methylcyclohexene using (**2**) and a variety of other catalysts. It is clear from this data that (**2**) is a highly efficient epoxidation catalyst and 80% conversion is observed before the first sample can be taken for g.l.c. analysis (~30 s) when the catalyst to alkene ratio is 1 : 100. Even at a ratio of 1 : 1000, 50% conversion is observed in 3 min. After this very rapid initial epoxidation, the rate drops dramatically and the remaining alkene is epoxidised slowly. We believe that, as with other epoxidation catalysts,[3] the β-ketophosphonate ligand is replaced by a small amount of diol side product and that this complex has a low activity for epoxidation.

Support for the suggestion that the lability of the carbonyl oxygen atom in (**2**) is responsible for the very high catalytic activity is given by the observation that (**3**), in which both



(1)



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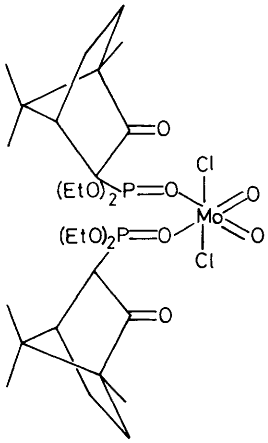

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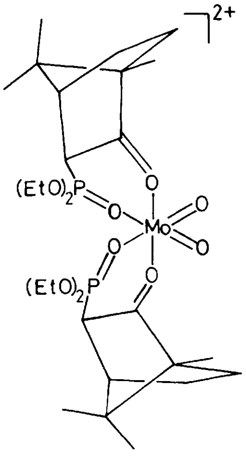

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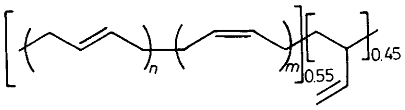

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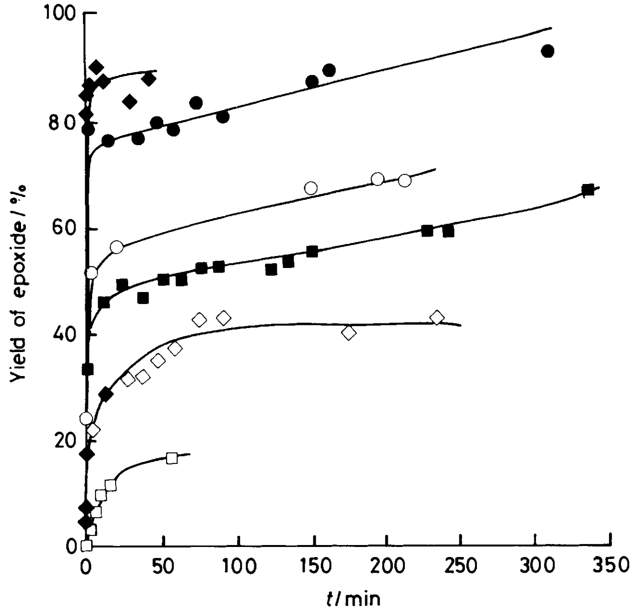

Figure 1. Epoxidation of 1-methylcyclohexene catalysed by various complexes. Conditions as Table 1, but varying catalyst and reaction time; ◆ (**2**), ● (**3**), ◇ (**3**) + 10 ligand [alkene: (**3**) = 1000 : 1], ■ (**2**) [alkene: (**2**) = 1000 : 1], □ (**3**) + 2 AgBF$_4$, ○ MoO$_2$Cl$_2$

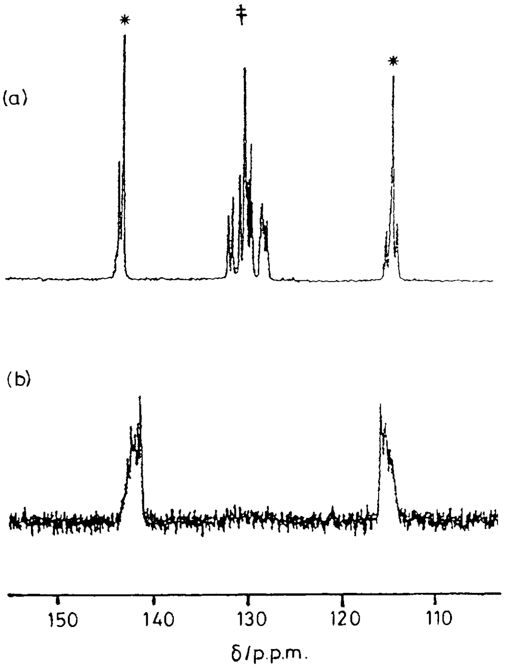

Figure 2. Olefinic region of the ^{13}C n.m.r. spectrum of (a) polybutadiene containing 45% vinyl double bonds and 55% of mixed *cis* and *trans* (backbone) double bonds. (b) The polymer of (a) after epoxidation using Bu^{t}OOH and (**2**) at 20 °C for 20 h. Integration of the ^{1}H n.m.r. spectrum shows 45% of the double bonds remained; 55% have been epoxidised. * Vinyl double bonds; ‡ backbone double bonds.

ligands are bound through the phosphoryl oxygen atoms and will therefore be less labile (at least if a dissociative exchange pathway is followed), is a less active catalyst than (**2**) (Figure 1). Similarly, suppression of dissociation of the β-ketophosphonate in (**3**) by addition of excess free ligand reduces the rate still further. Removal of the chloride ions from (**2**) by addition of AgBF$_4$, apparently to give (**4**), gives a system which has even lower activity. Presumably, the more acidic molybdenum centre in the dication makes the carbonyl oxygen atoms less labile than in (**2**) or (**3**).

As part of an interest in the selective functionalisation of polybutadiene [structure (**5**)] at either its backbone or terminal double bonds, we have studied its epoxidation using (**2**) and Bu^{t}OOH. Previous attempts to epoxidise similar polybutadienes using either organic[4,5] or catalytic[6] epoxidising systems have shown a preference for the backbone double bonds (*cis*-1,4 > *trans*-1,4 ≫ 1,2) but in no cases have very high selectivities been observed; the terminal double bonds start to epoxidise before all the backbone double bonds have reacted, or some of the backbone double bonds are left unreacted.

Table 1. Epoxidation of various alkenes catalysed by (**2**).[a]

Alkene	t/h	T/°C	Yield of epoxide[b]/%
Hex-1-ene[c]	24	35	70.6
Dodec-1-ene	24	35	45[d]
Styrene[e]	24	20	0
Cyclohexene	24	20	77.8
1-Methylcyclohexene	0.7	0	89
	24	20	100(52)[d,f]
(*R*)-(+)-Limonene	28	20	65[g]
Norbornene	24	20	20[c]
3-Methylbut-1-ene	24	20	—[h]
3,3-Dimethylbut-1-ene	24	20	25

[a] Molar ratio: alkene (100); (**2**) (1); Bu^{t}OOH (3 mol dm^{-3} in 2,2,4-trimethylpentane) (150); CH_2Cl_2 (1466). [b] G.l.c. yield unless otherwise indicated. [c] 1.08 molar ratio of (**2**). [d] Isolated yield, after work up. [e] 930 molar ratio of CH_2Cl_2. [f] 378 molar ratio of CH_2Cl_2. [g] As 1:1 mixture of diastereoisomers of 1-methyl-4-(1-methylethenyl)-7-oxabicyclo[4.1.0]heptane. [h] High conversion but not accurately measured.

We find that using (**2**) as a catalyst, *all* of the backbone double bonds are epoxidised within three hours at room temperature (see Figure 2) and that there is no further change in the next 70 hours.† The terminal double bonds remain unreacted. Using *e.g.* $[MoO_2(acac)_2]$ (acac = pentane-2,4-dionate), although much more forcing conditions are required (refluxing for 24 h), a less selective reaction is observed and substantial amounts of other products (diols?) are observed.

The origin of the very high selectivity of (**2**) in the epoxidation of polybutadiene is currently under study, but it is somewhat surprising that the terminal double bonds remain completely unreacted since studies on the model compounds, 3-methylbut-1-ene and 3,3-dimethylbut-1-ene show that they undergo epoxidation under similar conditions (Table 1). Using limonene, only the endocyclic double bond is epoxidised, but the conversion is only *ca.* 65%.

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† The apparent increase in complexity of the ^{13}C n.m.r. signals from the C atoms of the terminal double bonds on epoxidation requires further investigation. We note, however, that there are at least 6 different possible local environments for these double bonds in the parent and the product polymer so it is possible that some accidental degeneracies in the starting material are lifted in the product.

References

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