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Alkene Epoxidation catalysed by Camphor-derived β-Ketophosphonate Complexes of Molybdenum(VI)

Russell Clarke, Michael Gahagan, Raymond K. Mackie, Douglas F. Foster, David J. Cole-Hamilton * and (in part) Mairi Nicol and Andrew W. Montford
School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

New β-ketophosphonates (L) have been prepared from (*R*)- or (*S*)-camphor with various substituents on the phosphorus atom [EtO, (*R*)- or (*S*)-Bu^{s}O, Ph or binaphthoxy] and reacted with [MoO_2Cl_2] to form complexes [MoO_2Cl_2L]. These complexes have been used to give highly active catalysts for epoxidation of alkenes by Bu^{t}OOH. Very fast initial rates (*ca.* 400 catalyst turnovers in the first minute) gave way to much slower rates because the hemi-labile β-ketophosphonate is displaced by a diol ligand. In the presence of molecular sieves, the fast initial stage of the reaction is extended and for styrene, which gives low conversions followed by degradation in the absence of molecular sieves, styrene oxide can be formed with 98% conversion and 94% selectivity. It is demonstrated that both the Bu^{t}OOH and the catalyst bind to the molecular sieves, the latter with loss of the β-ketophosphonate ligand.

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Epoxides are important organic intermediates since they undergo ring-opening reactions with a variety of reagents to give mono- or bi-functional organic products. In general, epoxides can be prepared by oxidation using alkylhydroperoxides in the presence of high-valent early transition-metal catalysts.[1] We have recently reported[2] the synthesis of the complex [$MoO_2Cl_2L^1$] [L^1 = (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor] and shown that it is a highly active catalyst for the epoxidation of polymeric alkenes.[3] For polybutadienes that contain double bonds both in the polymer backbone and pendant from the main chain, this catalytic system shows high selectivity towards the functionalisation of the backbone double bonds, particularly if the reactions are carried out in the presence of molecular sieves.[3]

In this paper, we report the synthesis of a variety of other complexes containing β-ketophosphonates derived from camphor {(*R*)-(+)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one} in which we vary the substituents on the phosphorus atom as well as the chirality of these substituents and the chirality at camphor. The use of these complexes as catalysts for the epoxidation of simple alkenes is described and the effect of molecular sieves on the reactions, which can be dramatic especially for styrene as a substrate, is discussed. Preliminary results of some of this work have been communicated.[4,5]

Results and Discussion

Ligand Synthesis.—The β-ketophosphonates, L^1–L^6, shown in Scheme 1, were prepared by the method that we have previously described for (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor (L^1) and which was originally reported by Wiemer and co-workers.[6] All of the reactions proceeded smoothly, although it was necessary to synthesise the di(*sec*-butyl) phosphorochloridates. This was achieved by reaction of the relevant optically active butanol with PCl_3 in the presence of triethylamine to give the di(*sec*-butyl) chlorophosphonite which was then hydrolysed and treated with SO_2Cl_2 to give the desired product. The steps for the synthesis of (1*R*)-*endo*-(+)-3-{bis[(*S*)-(+)-*sec*-butoxy]phosphoryl}camphor are outlined in Scheme 1.

We also synthesised the related (binaphthyldiyldioxyphosphoryl)camphor (L^8), although in this case the phosphorochloridate could be synthesised directly from $POCl_3$ and binaphthol in the presence of triethylamine. Racemic binaphthol was used in these reactions but one diastereomer of the product could be isolated by fractional crystallisation. (1*R*)-*endo*-(+)-3-(Diphenylphosphoryl)camphor (L^7) was synthesised by oxidation of the corresponding (diphenylphosphino)-camphor[7] with H_2O_2 or by recrystallisation in air.

Table 1 Microanalytical data for new molybdenum complexes

	Found (%)		Calculated (%)	
Complex	C	H	C	H
[$MoO_2Cl_2L^2$]	34.3	5.0	34.5	5.2
[$MoO_2Cl_2L^3$]	40.4	6.0	39.8	6.1
[$MoO_2Cl_2L^4$]	39.7	6.2	39.8	6.1
[$MoO_2Cl_2L^5$]	39.1	5.9	39.8	6.1
[$MoO_2Cl_2L^6$]	38.6	5.5	39.8	6.1
[$MoO_2Cl_2L^7$]	47.8	4.4	47.9	4.6

Synthesis of Metal Complexes.—Complexes of the form [MoO_2Cl_2L] (L = L^1–L^7) were synthesised as reported previously[2] by direct reaction of L (Scheme 1) with [MoO_2Cl_2] (Table 1). Ligand L^8 was unreactive and no complex could be isolated, presumably because of its steric bulk.

All the ligands and complexes have been fully characterised by spectroscopic means (see Tables 2 and 3). The complexes all have *cis* oxo ligands and *trans* chlorides, as we have previously shown crystallographically for [$MoO_2Cl_2L^1$].[2]

Alkene Epoxidation Reactions.—All of the complexes show very high activities for the epoxidation of simple alkenes, although, since no asymmetric induction was observed in any of the reactions, detailed studies are only reported for representative examples of the complexes (Table 4). In all cases, high activity and selectivity towards the epoxidation of cyclic, di- and tri-substituted alkenes is observed, as expected for the addition of the electrophilic oxygen atom, and for limonene 100% selectivity towards epoxidation of the endocyclic (trisubstituted) alkene is obtained, the exocyclic alkene remained unreacted. The *cis* and *trans* isomers of limonene oxide are obtained in equal amounts. For terminal alkenes the reactions are slower and for styrene, no styrene oxide is apparent after 1 h of reaction. Close examination of the

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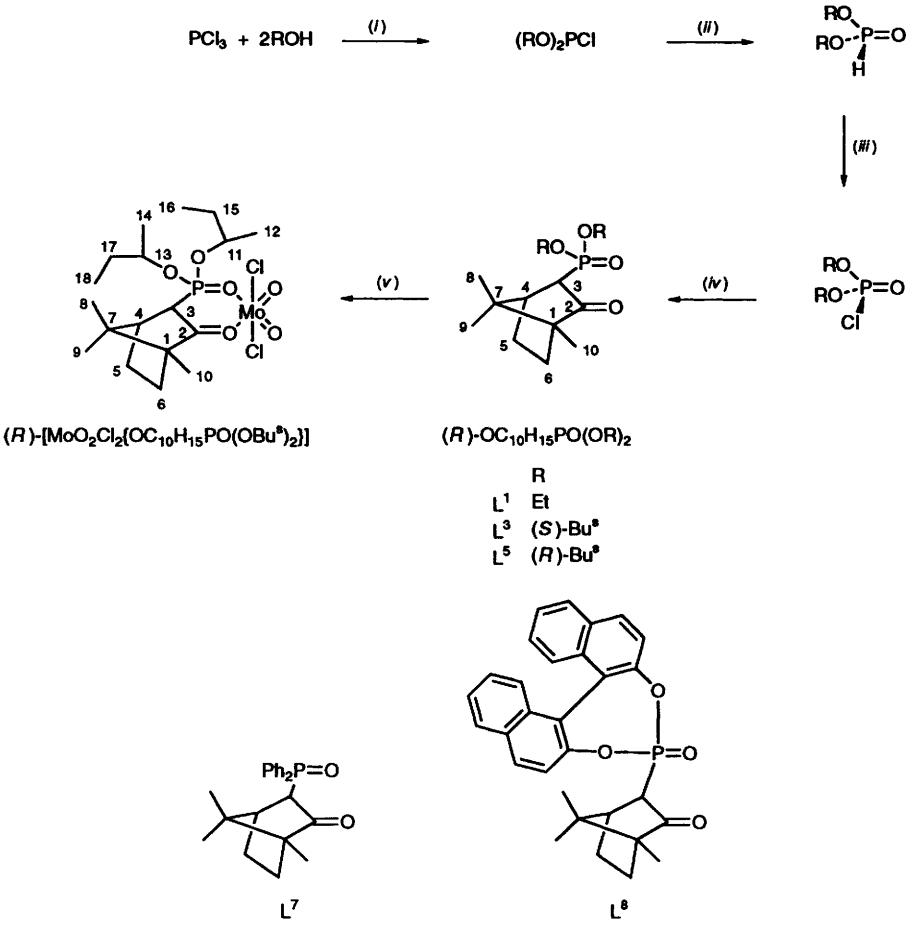

Scheme 1 Synthesis of β-ketophosphonates and their metal complexes. (*i*) NEt_3; (*ii*) H_2O; (*iii*) SO_2Cl_2; (*iv*) 3-lithiocamphor, $Li[NPr^i_2]$; (*v*) $[MoO_2Cl_2]$. The numbering scheme for the ethoxy ligands is identical to that shown with C(15)–C(18) replaced by H; (*S*)-$OC_{10}H_{15}PO(OR)_2$, R = Et L^2, (*S*)-Bu^s L^4 or (*R*)-Bu^s L^6

oxidation of styrene using $[MoO_2Cl_2L^1]$ shows that *ca.* 25% conversion to styrene oxide occurs in the first minute of the reaction but this then degrades mostly to benzaldehyde so that none of the styrene oxide remains after 1 h (Fig. 1).

In all cases, the catalysts show very rapid initial rates of conversion to the epoxide over the first 5 min (up to *ca.* 400 catalyst turnovers in the first minute) of the reaction but the rate then slows dramatically (see Fig. 2). We have observed this same type of reaction profile for a variety of different molybdenum complexes.[4] We have attributed[4,5] this fall off in rate to the presence of adventitious water in the system and like others[8,9] believe that this leads to ring-opened diols which replace the β-ketophosphonate on the metal to give a less active species. Indeed, we have subsequently shown $[MoO_2Cl_2L]$ are good catalysts for the ring opening of the epoxides by water.[10] The lower activity of the diol complexes than that of the β-ketophosphonate complexes for epoxidation may perhaps be explained because the β-ketophosphonates are hemi-labile (the carbonyl oxygen atom is held much more weakly than the phosphoryl)[2] so can readily provide a vacant site for co-ordination of the Bu^{t}OOH, whilst the diols will be more symmetrically and strongly bound.

Proton and ^{31}P NMR studies on $[MoO_2Cl_2L^1]$ in the presence of 1-methylcyclohexene, Bu^{t}OOH or both together indicate that L^1 remains co-ordinated to the metal for periods of at least 1 h but that longer reaction times (24 h) lead to its displacement from the metal centre.

Catalytic Reactions in the Presence of Added Molecular Sieves.—We suspected that adventitious moisture might be responsible for the observed fall off in the rate of the

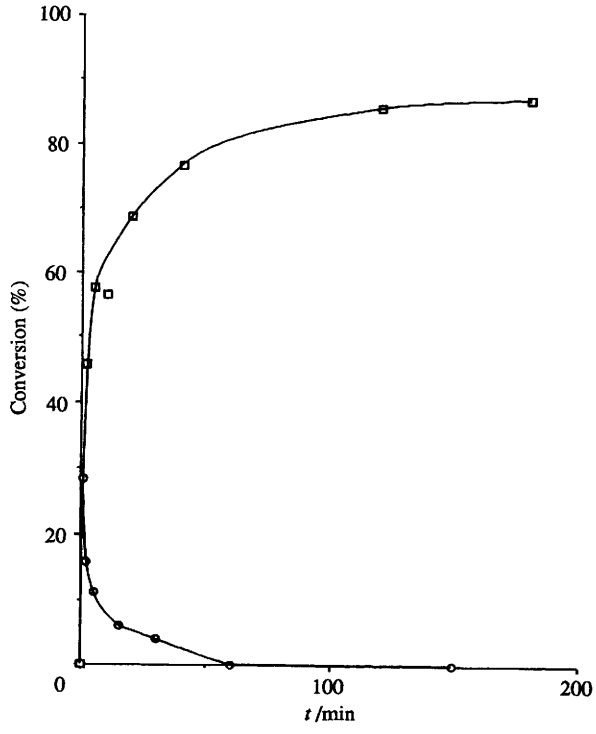

Fig. 1 Epoxidation of styrene catalysed by $[MoO_2Cl_2L^1]$ at room temperature, without (○) and with (□) molecular sieves

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Table 2 IR, ^{31}P and ^{1}H NMR data for new ligands and their molybdenum complexes[a]

Compound	ν(C=O)/ cm^{-1}	δ(^{31}P)	δ											
			C^3H	C^4H	C^5H_{endo}	C^5H_{exo}	C^6H_2	C^8H_3	C^9H_3	$C^{10}H_3$	$C^{11,13}H_n$	$C^{12,14}H_3$	$C^{15,17}H_2$	$C^{16,18}H_3$
L^2	1742	23.1	3.0 (dm, 1)[b]	2.35 (t, 1)	2.1 (m, 1)	1.9 (m, 1)	1.7 (m, 2)	0.85 (s, 3)	0.9 (s, 3)	1.0 (s, 3)	4.2 (m, 4)	1.35 (t, 6)		
L^3,L^6	1743	21.0	2.9 (dm, 1)[b]	2.3 (t, 1)	2.15 (m, 1)	1.9 (m, 1)	1.6 (m, 2)	0.8 (s, 3)	0.9 (s, 3)	1.0 (s, 3)	4.55 (m, 1) 4.65 (m, 1)	1.3 (m, 6)	1.6 (m, 4)	0.9 (m, 6)
L^4,L^5	1743	23.1	2.95 (dm, 1)[b]	2.35 (t, 1)	2.20 (m, 1)	1.9 (m, 1)	1.65 (m, 2)	0.85 (s, 3)	0.95 (s, 3)	1.0 (s, 3)	4.55 (m, 1) 4.65 (m, 1)	1.35 (d, 3) 1.40 (d, 3)	1.65 (m, 4)	0.95 (m, 6)
L^8		33.7	3.0 (dm, 1)	2.3 (t, 1)	2.5 (m, 1)	1.8 (m, 3)		0.7 (2, 3)	1.5 (s, 6)					7.25–8.05 (m, 12)[c]
$[MoO_2Cl_2L^2]$	1697	24.3	3.8 (dm, 1)[d]	2.5 (t, 1)	2.1 (m, 1)	1.9 (m, 1)	1.55 (m, 2)	0.9 (s, 3)	1.0 (s, 3)	1.1 (s, 3)	4.4 (m, 4)	1.4 (t, 3) 1.35 (t, 3)		
$[MoO_2Cl_2L^3]$ $[MoO_2Cl_2L^6]$	1697	21.1	3.8 (dm, 1)[d]	2.45 (t, 1)	2.15 (m, 1)	1.7 (m, 1)	1.9 (m, 2)	0.95 (s, 3)	1.0 (s, 3)	1.05 (s, 3)	4.85 (m, 1) 5.0 (m, 1)	1.4 (d, 3) 1.5 (d, 3)	1.7 (m, 4)	0.95 (m, 6)
$[MoO_2Cl_2L^4]$ $[MoO_2Cl_2L^5]$	1699	21.2	3.8 (dm, 1)[d]	2.45 (t, 1)	2.15 (m, 1)	1.65 (m, 1)	1.6 (m, 2)	0.9 (s, 3)	1.05 (s, 3)	1.1 (s, 3)	4.85 (m, 1) 5.05 (m, 1)	1.4 (m, 6)	1.65 (m, 4)	0.9 (m, 6)
$[MoO_2Cl_2L^7]$	1694	42.8	4.55 (dm, 1)	2.7 (t, 1)	1.5–2.0 (m, 4)			0.95 (s, 3)	1.0 (s, 3)	1.1 (s, 3)				7.5–8.0 (m, 10)[c]

[a] Expressed as δ (multiplicity, number of protons) for ^{1}H NMR data; assignments of C^8H_3, C^9H_3 and $C^{10}H_3$ are arbitrary; for other assignments see Scheme 1. [b] $J(PH) = 27.5$ Hz. [c] Aromatic protons. [d] $J(PH) = 32.2$ Hz.

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Table 3 ^{13}C NMR data for new β-ketophosphonate ligands*

	δ								
Ligand	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
L^2	58.9 (3.8)	211.3 (2.1)	50.7 (144.3)	46.2 (1.6)	23.0 (4.9)	29.7	49.9 (17.4)	18.7	19.4
L^3,L^6	58.9 (3.6)	211.4	51.4 (146.0)	46.4 (1.9)	22.9 (5.0)	29.7	46.8 (17.2)	18.8	19.4
L^4,L^5	58.9 (3.8)	211.3 (2.7)	51.2 (145.6)	46.3 (1.7)	22.9 (5.0)	29.6	46.8 (17.2)	18.7	19.4
	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	C^{16}	C^{17}	C^{18}
L^2	9.6	62.0 (6.3)	16.4 (6.1)	61.9 (7.0)	16.4 (6.1)				
L^3,L^6	9.7	75.1 (7.0)	21.1 (3.6)	74.8 (7.2)	20.9 (10.1)	30.6 (4.5)	9.5	30.4 (6.1)	9.3
L^4,L^5	9.7	75.3 (7.0)	21.5 (1.7)	74.7 (7.2)	21.0 (3.7)	30.7 (3.6)	9.34	30.4 (5.9)	9.29

* Recorded in $CDCl_3$ at 298 K; values in parentheses are J(PC)/Hz; assignments of C^8, C^9 and C^{10}, C^{11} and C^{13}, C^{12} and C^{14}, C^{15} and C^{17}, C^{16} and C^{18} are arbitrary.

Table 4 Yields of epoxide (%) from oxidations of alkenes by Bu^{t}OOH in the presence of $[MoO_2Cl_2L]$[a]

Substrate	L^1	L^3
Cyclohexene	77.8[b]	
1-Methylcyclohexene	74.7[c] (95.7)[c] 100[b]	61.7 (97.5)
Phenylethene	0 (80.0) (97.7)[b]	0 (61)
1-Methyl-1-phenylethene	12.5 (55.5)	
trans-1,2-Diphenylethene	56.3 (85) (100)[b]	
(*R*)-(+)-Limonene[d]	68.8 (87)	74.0 (91.0)
Norbornene[e]	20.0[b]	
Hex-1-ene	70.6[b,f]	
Dodec-1-ene	45.0[b,f]	
3,3-Dimethylbut-1-ene	25.0[b]	

[a] T = 293 K, 1 h, numbers in parentheses are for reactions carried out in the presence of molecular sieves. For conditions, see Experimental section. [b] After 24 h. [c] At 273 K. [d] (*R*)-(+)-1-Methyl-4-(1-methylethenyl)cyclohex-1-ene, only the endocyclic double bond is epoxidised. In the presence of $[MoO_2Cl_2L^7]$ yield of epoxide is 83.7%. [e] Bicyclo[2.2.1]hept-1-ene. [f] At 308 K.

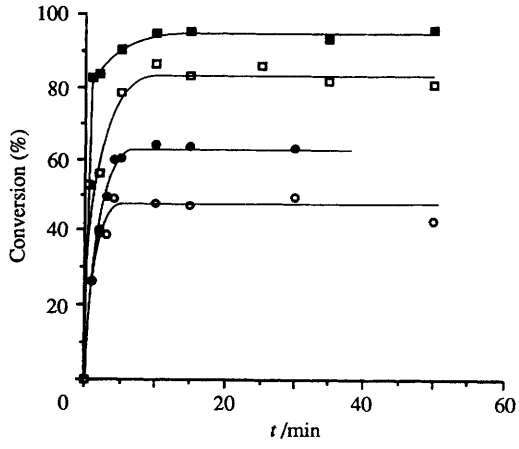

Fig. 2 Epoxidation of 1-methylcyclohexene catalysed by $[MoO_2Cl_2L^1]$ at 0 °C at various substrate:catalyst ratios with and without molecular sieves. (○) 1000:1, no molecular sieves; (●) 1000:1, with molecular sieves; (□) 100:1, no molecular sieves; (■) 100:1, with molecular sieves

epoxidation reaction after *ca.* 5 min, and as Sharpless and co-workers[11] have used molecular sieves in their epoxidation reactions so as to render them catalytic, we carried out epoxidation reactions in the presence of molecular sieves (powdered 4A). For all alkenes there was indeed a major improvement in the number of catalyst turnovers that were observed in the first (fast) stage of the reaction although there was still some fall off in reaction rate with time (see Table 4 and Fig. 2). The most dramatic effects were observed for reactions of styrene where the yield increased dramatically and indeed 98% conversion with 94% selectivity to styrene oxide could be observed after 24 h with a 1:100 catalyst:substrate ratio (Fig. 1). This reaction was carried out at room temperature and represents one of the most selective procedures for the production of styrene oxide yet reported. The best other molybdenum-based system (98% conversion, 94% selectivity) involves molybdenum octanoate in the presence of $B(OPr^i)_3$ as the catalyst and cumene hydroperoxide as the oxidising agent, but temperatures in the range 100–125 °C are required.[12] Systems containing other metals that can give high conversions and selectivities for styrene epoxidation at room temperature include porphyrin complexes of manganese[13] (95% conversion, 98% selectivity) or iron[14] (97% conversion).

Although one role of the molecular sieves is indeed to scavenge water in the system we have carried out detailed studies (Table 5) which show that it also performs a variety of other functions. Of particular importance is the observation that the catalyst binds to the molecular sieves and, indeed, we have shown that if $[MoO_2Cl_2L^1]$ is stirred with molecular sieves in CH_2Cl_2 and the solution filtered, pure L^1 can be obtained on evaporation of the solvent. This shows that the ligand is expelled from the catalyst by the molecular sieves. Since $[MoO_2Cl_2]$, which is of low solubility in CH_2Cl_2, itself shows lower activity for the epoxidation of styrene or cyclohexene in the presence of molecular sieves than does $[MoO_2Cl_2L^1]$, we conclude that the β-ketophosphonate simply acts as a solubilising agent which aids the delivery of $[MoO_2Cl_2]$ to the surface of the molecular sieves, but is sufficiently labile to be removed rapidly once the complex comes into contact with the surface of the sieves. The sieves also appear to bind the Bu^{t}OOH but both the $[MoO_2Cl_2]$ and the Bu^{t}OOH must be bound close to one another for successful epoxidation to occur. Interestingly, anhydrous $MgSO_4$ also appears to prevent the degradation of the styrene oxide that is formed, although the catalyst lifetime is short, providing only 30% conversion before the reaction stops. Silica is not effective as a support or drying agent in this reaction.

Conclusion

We conclude that the new complexes $[MoO_2Cl_2L]$, where L is a β-ketophosphonate derived from camphor, are highly effective catalysts for the epoxidation of alkenes, and show high chemoselectivity towards more electron-rich double bonds. Activities and, in some cases, selectivities are increased even further if molecular sieves are added but the active catalyst in these cases not only is bound to the sieves but also loses the β-ketophosphonate ligand. In the presence of sieves, $[MoO_2Cl_2L^1]$ proves to be one of the most effective catalysts so far reported for the conversion of styrene to styrene oxide.

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Table 5 Effect of different reaction protocols on the epoxidation of styrene catalysed by $[MoO_2Cl_2L^1]$

Protocol*	Time/h	Conversion to epoxide (%)
1 S + St + O + C	0.02	25
	1.0	0
2 Sv + S + St + O + C	0.02	45
	24	97.7
3 Sv + S + St + O + [C + S + Sv]F	18	0
4 S + St + O + CSv	18	20
5 Sv + S + St + [Sv + S + O]F + C	1.0	22
	48	44
6 Sv + S + St + O + CSv	18	0
7 Sv + S + C + St + O	24	43.4
	144	69.5
8 Sv + S + O + St + C	24	54.5
	144	81.3
9 Sv + S + O + [Sv + S + St]F + C	0.02	47
	24.0	98
10 Si + S + St + O + C	0.02	0
	1.0	0

* S = CH_2Cl_2, St = styrene, O = Bu^{t}OOH, C = catalyst, Si = silica, Sv = molecular sieves; [ ]F = the filtrate from stirring together the components shown in brackets; CSv = the solid obtained from filtering a solution of sieves, solvent and catalyst. The reagents were added in the order shown in each case.

Experimental

Microanalyses were by the University of St. Andrews Materials Analysis Service, NMR spectra were recorded at 298 K in $CDCl_3$ on Brüker Associates AM 300 or Varian Gemini (200 MHz) spectrometers operating in the Fourier-transform mode with (for ^{13}C and ^{31}P) noise proton decoupling; IR spectra on a Perkin-Elmer PE 1710 spectrometer and gas–liquid chromatographs on a Pye-Unicam 4500 chromatograph containing a Hewlett-Packard CPSIL 19CB GC column with N_2 carrier gas (40 cm^3 min^{-1}) and a flame-ionisation detector. Optical rotations were measured at ambient temperature on an Optical Activity AA-1000 polarimeter in a 1 dm path length cell.

All starting materials except $[MoO_2Cl_2]$ (Lancaster Synthesis) were purchased from Aldrich and were used as received. All solvents were dried by distillation from sodium diphenylketyl [tetrahydrofuran (thf), light petroleum (b.p. 40–60 °C), diethyl ether and toluene] or CaH_2 after pretreatment with P_2O_5 (CH_2Cl_2). They were thoroughly degassed before use. All manipulations were carried out under nitrogen that was purified by passing through a Cr^{2+}–SiO_2 column using standard Schlenk-line and catheter-tubing techniques. (1*R*)-*endo*-(+)-3-(Diethoxyphosphoryl)camphor, L^1, ($[\alpha]_D$ = 144.68°) and $[MoO_2Cl_2L^1]$ were prepared by previously described methods.[2]

Di[(S)-(+)-sec-*butyl*]*chlorophosphine*.—(*S*)-(+)-Butan-2-ol (2.2 cm^3, 0.026 mol) was added dropwise *via* a catheter to a cooled solution of phosphorus trichloride (1.1 cm^3, 0.013 mol), triethylamine (3.7 cm^3, 0.026 mol) and diethyl ether (20 cm^3) with stirring. This solution was allowed to stir for 24 h after which time the triethylammonium hydrochloride was removed by filtration through Hyflosupercel. The filtrate was concentrated on a rotavapour, to give a colourless oil. Yield 1.7 g, 59%. Normally, this compound was not isolated, but instead immediately hydrolysed to the corresponding phosphite.

Di[(*R*)-(−)-*sec*-butyl]chlorophosphine was similarly prepared from (*R*)-(−)-butan-2-ol.

Di[(S)-(+)-sec-*butyl*] *Phosphite*.—To a large excess of ice was added di[(*S*)-(+)-*sec*-butyl]chlorophosphine (2 g, 0.0094 mol) in anhydrous diethyl ether (20 cm^3) with stirring. After 2 h the water was removed and the organic layer was washed with sodium carbonate (1 mol dm^{-3}, 2 × 20 cm^3). The organic layer was then dried over magnesium sulfate, filtered, evaporated and purified by distillation to give a clear liquid. Yield 1.2 g, 66.7%. NMR: ^{31}P, δ 4.71 s; ^1H, δ 0.95 (t, 6 H, *Me*CH_2), 1.4 (d, 6 H, *Me*CH), 1.7 (m, 4 H, CH_2), 4.5 (m, 2 H, CH) and 6.9 [d, 1 H, *J*(PH) = 688.7 Hz, PH].

Di[(*R*)-(−)-*sec*-butyl] phosphite was similarly prepared from di[(*R*)-(−)-*sec*-butyl]chlorophosphine. Yield 1.1 g, 61.1%.

Di[(S)-(+)-sec-*butyl*] *Phosphorochloridate*.—Sulfuryl chloride (1.8 g, 0.0134 mol) was added slowly *via* a catheter to a stirred solution of di[(*S*)-(+)-*sec*-butyl] phosphite (2.6 g, 0.0134 mol) in anhydrous dichloromethane (20 cm^3) with stirring. This solution was allowed to stir for 2 h, after which the solvent was removed *in vacuo*, leaving a pale yellow oil. Yield 2.22 g, 72.6%. NMR: ^{31}P, δ 21.67 s; ^1H, δ 1.0 (t, 6 H, *Me*CH_2), 1.5 (d, 6 H, *Me*CH), 1.7 (m, 4 H, CH_2) and 4.6 (m, 2 H, CH).

Di[(*R*)-(−)-*sec*-butyl] phosphorochloridate was similarly prepared from di[(*R*)-(−)-*sec*-butyl] phosphite. Yield 2.19 g, 68.6%.

(±)-1,1′-*Binaphthyl*-2,2′-*diyl Phosphorochloridate*.—To a slurry of (±)-1,1′-bi-2-naphthol (5 g, 0.017 mol), $POCl_3$ (3.17 g, 0.021 mol) and CH_2Cl_2 (30 cm^3) was added triethylamine (4.18 g, 0.41 mol) dropwise at a rate that maintained gentle reflux. The solution was stirred for 1 h and extracted with water (20 cm^3). The organic phase was dried with $MgSO_4$ and evaporated to dryness to leave a white microcrystalline solid. Yield 7.47 g, 87.5%.

(1R)-endo-(+)-3-{*Bis*[(S)-sec-*butoxy*]*phosphoryl*}-*camphor*, L^3.—A solution of (1*R*)-*endo*-(+)-camphor (1.3 g, 0.0088 mol) in anhydrous thf (14.5 cm^3) was added dropwise *via* a catheter to a stirred solution of lithium diisopropylamide [1.1 equivalents, prepared *in situ* from diisopropylamine (1.4 cm^3) and *n*-butyllithium (6.2 cm^3, 1.6 mol dm^{-3})] in thf (5.5 cm^3) at −65 °C. After 45 min, the resulting enolate was treated with di[(*S*)-(+)-*sec*-butyl] phosphorochloridate (2.2 g, 0.0097 mol) and the mixture was allowed to warm to 0 °C over the course of 50 min. After this, the mixture was cooled to −75 °C, and transferred to a solution of lithium diisopropylamide (2.2 equivalents in 10.9 cm^3 of thf). The resulting solution was allowed to warm to 10 °C over 2 h. A solution of glacial acetic acid in diethyl ether (1 mol dm^{-3}, 4 equivalents) was added slowly *via* a catheter to the cooled reaction mixture, and the resulting solution was filtered through Hyflosupercel to remove the precipitate. The filtrate was then washed thoroughly with concentrated HCl (3 × 25 cm^3) then sodium carbonate solution to remove any remaining salt, and concentrated on a rotavapour before purification using Kuglerorh distillation. Yield 1.2 g, 39.4%; $[\alpha]_D$ = +165.15°.

Similarly prepared were: (1*R*)-*endo*-(+)-3-{bis[(*R*)-*sec*-butoxy]phosphoryl}camphor, L^5, from di[(*R*)-(−)-*sec*-butyl] phosphorochloridate; yield 0.9 g, 29.6%, $[\alpha]_D$ = 107.2°; (1*S*)-*endo*-(−)-3-{bis[(*S*)-*sec*-butoxy]phosphoryl}camphor, L^4, from (1*S*)-*endo*-(−)-camphor; yield 0.9 g, 29.6%, $[\alpha]_D$ = −93.54°; (1*S*)-*endo*-(−)-3-{bis[(*R*)-*sec*-butoxy]phosphoryl}-camphor, L^6, from (1*S*)-*endo*-(−)-camphor and di[(*R*)-(−)-*sec*-butyl] phosphorochloridate; yield 1.3 g, 42.4%, $[\alpha]_D$ = −167.2°; (1*S*)-*endo*-(−)-3-(diethoxyphosphoryl)camphor, L^2, from (1*S*)-*endo*-(−)-camphor (0.37 g, 2.43 mmol) and diethylphosphorochloridate (0.4 cm^3, 2.67 mmol); yield 0.21 g, 30.1%, $[\alpha]_D$ = −136.04°; and (1*R*)-*endo*-(+)-3(1,1′-binaphthyl-2,2′-diyldioxyphosphoryl)camphor, L^8 from (1*R*)-*endo*-(+)-camphor (5 g, 0.033 mmol) and 1,1′-binaphthyl-2,2′-diyl phosphorochloridate (13.23 g, 0.036 mol); the initial product was a 1:1 mixture of diastereomers, but one of these could be isolated by recrystallisation of the pale yellow solid from ethanol.

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(1R)-endo-(+)-3-(*Diphenylphosphoryl*)*camphor*, L^7, was prepared from (1*R*)-*endo*-(+)-3-(diphenylphosphino)camphor [7] by recrystallisation from ethanol in air. Yield 1.34 g, 76%.

Preparation of Molybdenum Complexes.—The complex $[MoO_2Cl_2]$ (1.5 g, 7.54 mmol) was dissolved in dry thf (30 cm^3). The phosphorylcamphor ligand (7.54 mmol) was added. After stirring for 1 h, the thf was removed *in vacuo* to leave an oily residue. Treatment with dry diethyl ether (15 cm^3) gave a solid which was washed with diethyl ether (2 × 5 cm^3). Yield 70–85%.

Reaction with Molecular Sieves.—The catalyst $[MoO_2Cl_2L^1]$ (0.5 g) was dissolved in CH_2Cl_2 and treated with pre-dried molecular sieves (10 g). After filtration, the supernatant liquid was evaporated to dryness to give a white solid. This was identified as L^1 by comparison of its IR, ^1H and ^{31}P NMR spectra with those of an authentic sample.

Catalytic Epoxidation Reactions.—In a typical reaction, $[MoO_2Cl_2L^1]$ (0.04 g, 8.3 × 10^{-5} mol) was added to CH_2Cl_2 (5 cm^3) containing the substrate, *e.g.* 1-methylcyclohexene (1 cm^3, 8.3 mmol), and Bu^tOOH [4.2 cm^3, 3 mol dm^{-3} in 2,2,4-trimethylpentane (12.5 mmol)] cooled to 0 °C. Samples (0.3 cm^3) were taken at selected time intervals. These were treated with PPh_3 (0.01 g) to stop the reaction and analysed by GLC.

For reactions in the presence of molecular sieves, the sieves (0.5 g) were first heated *in vacuo* at 100 °C for 5 h, the reaction mixture of the same composition as that described above without the catalyst was added and the resulting slurry stirred at 0 °C for 0.3 h. The catalyst was added and the reaction was sampled and analysed as described above.

For the determination of optical yields, the products were analysed directly by GLC (limonene oxide) or were separated by fractional distillation and analysed by ^1H NMR spectroscopy in the presence of 1-(9-anthryl)-2,2,2-trifluoroethanol [15] (other substrates). Good separations of the resonances from different enantiomers were obtained but there was no evidence for chiral induction.

Acknowledgements

We thank BP (M. N.), Rhône-Poulenc and the SERC (R. C.) for studentships and the SERC for a Fellowship (to D. F. F.).

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Received 24*th October* 1994; *Paper* 4/06509C

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