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REVIEW

Organometallic Compounds in Asymmetric Synthesis: Oxygen Atom Transfer

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Keywords: chiral synthesis; asymmetric reactions; oxygen atom transfer

CONTENTS

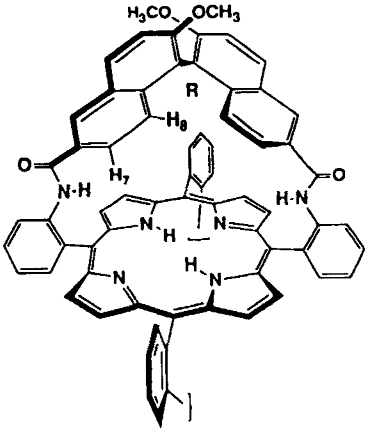
1 INTRODUCTION

Many interesting asymmetric oxygen atom transfer methods are purely organic, such as the Davis chiral oxaziridine method of epoxidation, enolate and sulfide oxidation,[1–3] the Wynberg,[4] Colonna[5] or Julia[6] asymmetric Weitz–Scheffer systems for epoxidation of electron-poor alkenes, and microbial or enzymic methods,[7,8] but the most useful methods involve organometallic compounds. Some can now be considered as synthetic tools, such as the Sharpless asymmetric dihydroxylation of isolated alkenes, the Jacobsen asymmetric epoxidation method, the Kagan oxidation of sulfides or the well-known Sharpless asymmetric epoxidation of allylic alcohols.

2 ASYMMETRIC OXYGEN ATOM TRANSFER ON CARBON ATOMS

2.1 Asymmetric hydroxylation

In 1990, Groves and Viski[9] described the first system for catalytic asymmetric hydroxylation of alkanes to alcohols using a metal complex, namely an iron or manganese complex of a vaulted porphyrin with two binaphthyl bridges (**1**), and iodosylbenzene as oxygen source. The results with this system are impressive: an enantiomeric excess of 20–72% for tetrahydronaphthalene!



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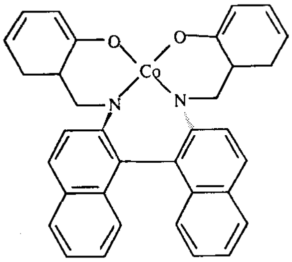

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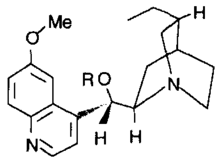
Similarly, a chiral salen complex of cobalt (**2**)[10] has been found to catalyze the oxidation of styrene with dioxygen to yield optically active 1-phenylethanol (38% ee).

2.2 Asymmetric dihydroxylation (ADH)

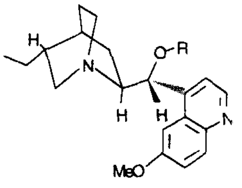
Since the first report by Hentges and Sharpless in 1980[11] of the asymmetric osmylation of isolated alkenes to yield 1,2-diols, many studies have been devoted to this area, which has become one of the most significant successes of asymmetric catalysis.[12]

2.2.1 Alkaloid-based systems

The original Sharpless system for asymmetric dihydroxylation[11] uses stoichiometric amounts of osmium tetraoxide and a chiral ligand, derivatives of quinidine (**3**) or quinine (**4**), with R = acetyl (Ac).



dihydroquinidine derivatives, **3**



dihydroquinine derivatives, **4**

Dihydroquinine (DHQ) and dihydroquinidine (DHQD) are actually diastereoisomers, but act as pseudoenantiomers because they have opposite chirality at four of the five asymmetric carbons (the ethyl-bearing carbons remove from the quinuclidine nitrogen having the same chirality). The quinidine derivatives give the best enantioselectivities (5–94% ee). The quinine derivatives afford diols of slightly lower enantioselectivities but of opposite chirality.

By modifying the R group on alkaloid derivatives, Sharpless *et al.* have been able to vastly improve the performance of this system. The modifications have led to several classes of efficient ligands (Fig. 1): the acyl family *p*-chlorobenzoate derivatives[13] (the CLB class) and the indolinylcarbamoyl derivatives[14] (the IND class); for the aromatic ether family[15] phenanthryl derivatives[16, 17] (the PHN class), 4-methylquinolyl derivatives[16, 17] (the MEQ class) and recently phthalazyl[18] (the PHAL class) and pyrimidyl[19] (the PYR class) derivatives.

The performance of the system using the PHAL, PYR and IND classes of ligands significantly surpasses the performance of those using the other three. Almost all of the possible dihyd-

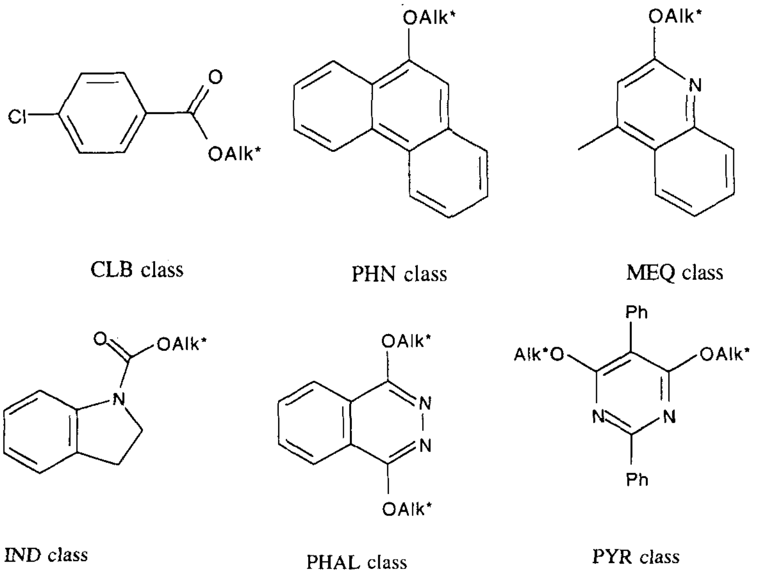
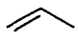
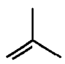
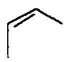
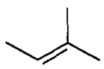
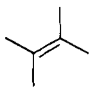


Figure 1 Classification of ligands. Alk*OH = dihydroquinine (DHQ) or dihydroquinidine (DHQD).

Table 1 Ligand preference as a function of alkene substitution pattern

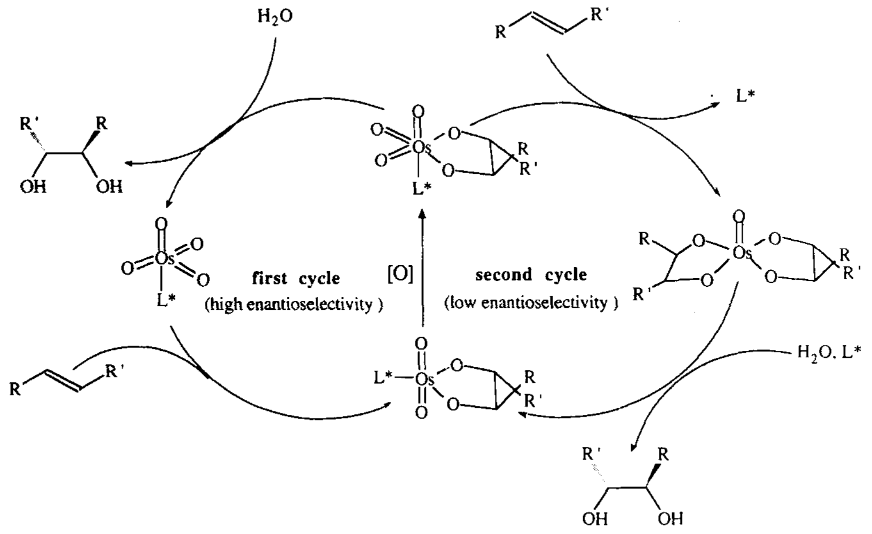
	Alkene substitution patterns					
						
Preferred ligand	PYR PHAL	PHAL	IND	PHAL	PHAL	PYR PHAL
ee range (%)	80–97	70–97	20–80	90–99.8	90–99	20–97

roxylations can be carried out with good to excellent enantioselectivities, except notably those of some *cis*-disubstituted alkenes, if the chiral alkaloid ligand is correctly chosen[13–20] (see Table 1). Even tetrasubstituted alkenes can be dihydroxylated in good yields, and with interesting levels of enantioselectivity.[20, 21]

Recently, Sharpless and co-workers showed that it is possible to increase the enantioselectivities obtained using the PHAL ligands[22] by changing the ethyl group of the quinuclidine moiety to a bulkier alkenyl (ee of 1,2-dihydroxydecane obtained by ADH of 1-decene increases from 84% to 88%) or ester group (ee up to 88%), or by changing the methoxy group of the quinoline part of the ligand to another, bulkier alkoxy group (ee up to 92% with isopentyloxy substituents on quinoline in 1-decene dihydroxylation).

The Sharpless group was able to make these systems catalytic with 13.4 mol % ligand and 0.2 mol % OsO_4 by using *N*-methylmorpholine *N*-oxide as reoxidant.[13] The yields are good (over 80%) but the enantioselectivities are always lower than for the stoichiometric reactions. Especially disapponting was the case of non-aromatic alkenes (ee < 20%), but it is possible to reach enantioselectivities close to those obtained under stoichiometric conditions by adding tetraethylammonium acetate (TEAA) and slowly adding the alkene to the oxidant system.[23–25] Sharpless and co-workers proposed a mechanism involving a second catalytic cycle of low enantioselectivities, which explains the varying experimental results and especially the role of addition of TEAA and of slow addition of the alkene[13] (see Scheme 1). This mechanism was later given further support by isolation and characterization by X-ray analysis of different intermediates.[26, 27]

Tsuji and co-workers reported the convenient



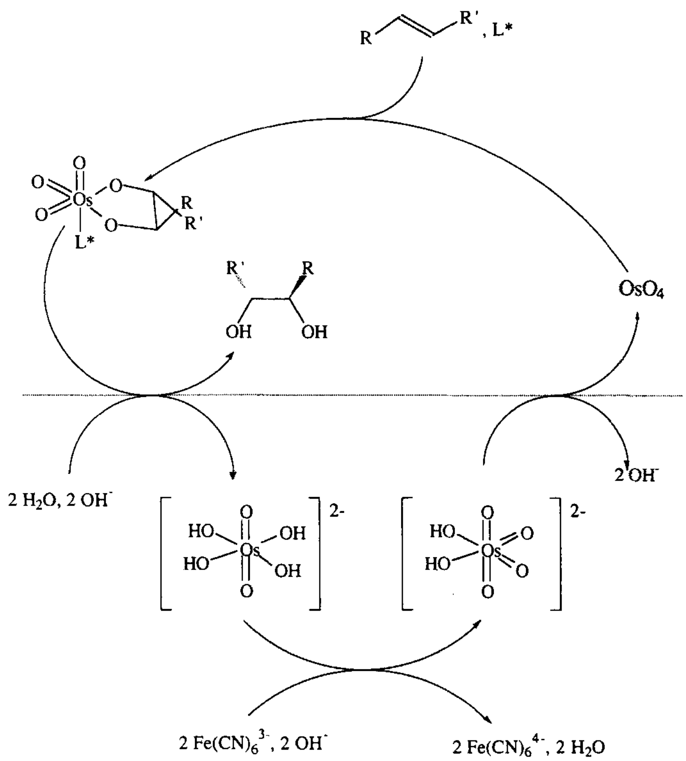
Scheme 1

and efficient use of potassium ferricyanide as reoxidant in the osmylation reaction in 1:1 mixture of water and t-butanol with sodium carbonate.[28] This new reoxidizing system was used with great success in the Sharpless asymmetric dihydroxylation reaction:[29] the enantioselectivities of the stoichiometric reaction can be reached without slow addition of the alkene but with high yields (85–95%). The success of this approach is due to the separation of the osmylation reaction and the osmium reoxidation in this biphasic system.[30] The osmylation occurs in the organic upper layer. The osmium reoxidation reaction takes place in the aqueous phase only after hydrolysis of the osmium(VI) glycolate, completely suppressing the second catalytic cycle described above (see Scheme 2).

All the improvements described above make the Sharpless asymmetric dihydroxylation (ADH) system of particular interest because:

(1) A large range of alkenes can be successfully dihydroxylated with high yields and enantioselectivities
(2) Either diol enantiomer can be made, depending on the choice of ligand in the system (DHQ or DHQD derivatives). Furthermore, for double diastereoselectivity of chiral alkenes, the matched and mismatched reactions can be achieved.
(3) The amount of osmium can be decreased in most cases to 0.1 mol %, reducing the amount of ligand to 1 mol % (a commercial mixture of reoxidant, ligand and osmium salt in the appropriate proportions can be purchased from Aldrich as AD-mix-α and AD-mix-β, according to the alkaloid used). For alkenes of low reactivity, increasing the amount of ligand or osmium often allows the reaction to proceed.[12, 31-33]
(4) All the components are commercially available and are relatively inexpensive, making this reaction particularly convenient.

The Sharpless ADH reaction was tested on number of different classes of alkene substrates: protected α,β-unsaturated aldehydes[34] (ee > 90%), dienes[35-37] (74–99% ee), and in particular on squalene,[38, 39] β,γ and γ,δ-unsaturated esters which yield the corresponding lactones[40]



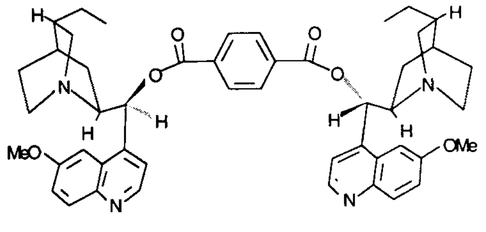
Scheme 2

(92–99% ee), α-substituted styrene derivatives[41] (0–97%), silyl and methyl enol ethers which yield α-hydroxyketones[42] (79–99% ee), enynes[43] (38–97% ee), aryl allyl ethers[44] (28–95% ee), α,β-unsaturated ketones[32] (82–98% ee), protected α,β- and β,γ-unsaturated amides[31] (93–98% ee), N-di-butoxycarbonyl allylic and homoallylic amines[33] (34–97% ee) vinyl and allylsilanes which yield secondary allylic alcohols (35–95% ee[45,46] or 6–88% ee[47]), allylic alcohols (36–93% ee)[48] and derivatives (11–91% ee),[49] *trans*-1-trimethylsilyl-3-alken-ynes[50] (96.5% ee) which yield furfuryl alcohols after hydromagnesiation, steroids,[51] terpene acetates[52,53] and even recently on buckminsterfullerene, C_{60}.[54] The reaction was also applied successfully to double diastereoselection of chiral alkenes.[34,55,56]

The diols obtained can be transformed into a variety of reactive derivatives (notably in the last five years, cyclic sulfates[57–59] and sulfites,[60] sulfonates,[61–63] cyclic orthoacetates[61,64] and carbamates[65]) leading to aminoalcohols, aziridines, diamines, etc.

The alkaloid-based ADH reaction has already been used to create the necessary chiral centers in numerous syntheses of natural products or drugs: anthelmintic agent hizymicin,[66] cardiac drug (+)-diltiazem,[61] halichondrin B,[67] immunodepressant FK-506,[68] anticancer taxol and taxotere RP 56976 side chains,[69,70] brassinolide,[71] disparlure and isomers,[72] beer aroma constituent 7,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane,[73] (−)-carnitine and (−)-GABOB,[74] (+)-coriolic acid,[75] tetroses,[76] (−)-5-deoxyjuglomycin,[77] (+)-*exo*-brevicomin,[78] 2,3-oxidosqualene,[79] (+)-goniopyrone,[80] antibiotic diolmycin A1,[81] juvenile hormone III[82] and its bisepoxide,[83] gerardiasterone,[84] (*S*)-fenfluramine,[85] WCR sex pheromone and antibiotic (−)-A26771B,[86] amino-acids,[87] castanospermine,[88] carbohydrates[89] etc.

The reaction has also been applied to kinetic resolution of racemic isolated alkenes. The first example, reported by Ward and Procter[90] had moderate success (selectivity factor $k_f/k_s = 1.7$) on allylic silanes with the PCB class. Lohray[91] successfully tested a new class of alkaloid derivatives (C_2) in the kinetic resolution of allylic acetates ($k_f/k_s = 3–25$). The C_2 class is superior to the PHAL class but not to the PCB class for this particular use.[92]



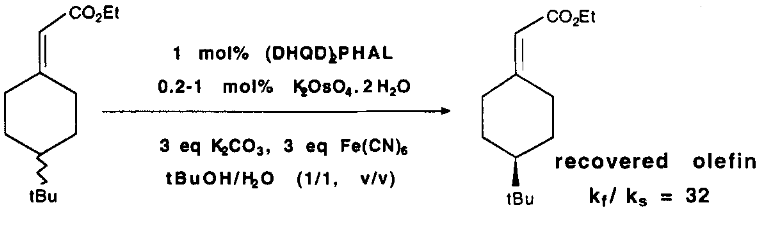
C_2-DHQD

Recently Sharpless demonstrated the efficiency of the PHAL derivatives for the kinetic resolution of chiral benzylidene (Eqn [1]).[93] The Sharpless ADH was applied also to kinetic resolution of racemic fullerene C_{76},[94] yielding the first sample of enantiomerically enriched C_{76} (97% ee).

It should be noted that some polymer-supported versions of Sharpless AD systems have been realized on polyacrylonitrile,[95,96] polystyrene[97] or polystyrene/polydivinylbenzene copolymer[98] supports. These systems are interesting because of an easy recovery of the chiral ligand by simple filtration, wash-up or centrifuging; the osmium–ligand complex appears to be strong enough to keep almost all the osmium on the polymer support during this ligand recovery process.[96,97] Provided that the alkaloid is kept far enough away from the polymer skeleton by a sufficiently long spacer,[95,98] and the amount of alkaloid incorporated is kept low[95–98] (<10%), the efficiency of this supported polymer can be good in term of yields and enantioselectivities (ee as high as 93%,[81] compared with 99% for t-stilbene with the homogeneous version).

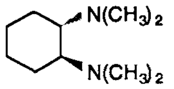
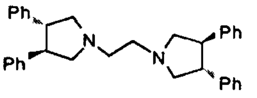
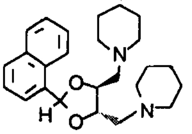
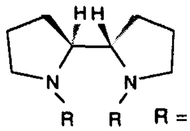
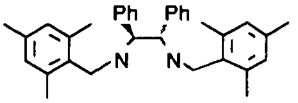
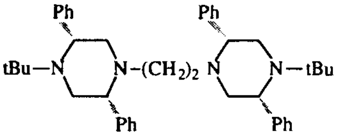
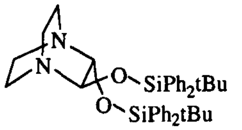
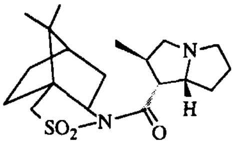
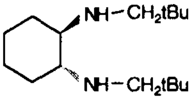
2.2.2 Other systems

Many other chiral amines have been used by different researchers as ligands for asymmetric



[1]

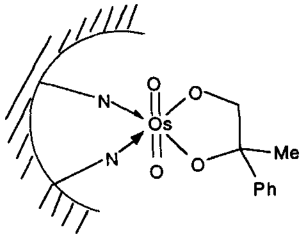
Table 2 Chiral amines used as ligands in asymmetric dihydroxylation

Chiral amine	ee (%)	Temperature/Conditions[a]	References
	34–86	RT/S	100
 6	83–99	−100 °C/S	101–104
	90	−100 °C/S	105
 R = neohexyl	88–100	−78 °C/S	106–109
 6	82–98	−90 °C/S	110
	12–98	−78 °C/S	111
	12–41	RT/C	112
	22–73	RT/C	113
	64–99	−90 °C/S	114

[a] RT, room temperature; S, stoichiometric in ligand; C, catalytic in ligand.

dihydroxylation. The results, often very interesting (ee over 90% in many cases) are summarized in Table 2. Most of them are diamines which form very strong complexes with osmium tetraoxide which are more reactive towards alkenes (yields and kinetics are still good down to −100 °C in most cases) than the analogous complexes with monoamines, such as alkaloid derivatives. But in all cases, stoichiometric amounts of ligand and osmium are necessary. Recently catalytic systems were described[112,113] which use non-alkaloid monodentate amines such as chiral 1,4-diazabicyclo[2.2.2]octane (DABCO) or chiral isoxazolidines, but the enantiomeric excesses of the diol product are still relatively low.

An osmium(VI) complex (**5**) bound on protein was also used to catalyze the ADH reaction.[99]



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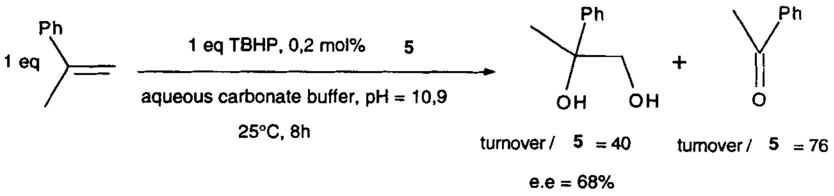
The enantioselectivities are very different, depending on the substrate (ee is from 6 to 68%) but can reach an interesting level, for example for α-methylstyrene (Eq. [2]).

Tomioka's ligand (6) and Corey's ligand (7) have been used in the synthesis of anthracyclic antibiotics[115] and cephalostatin analogs[116] respectively.

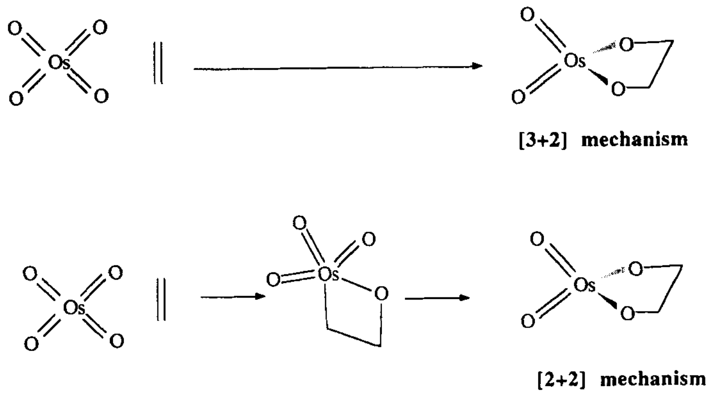
2.2.3 Mechanistic aspects

The mechanism of dihydroxylation of alkenes is still much debated.[117] The first question is whether the two carbon–oxygen bonds are formed in a concerted way ([3 + 2] mechanism)[118–120] or by a two-step mechanism via a metallaoxetane intermediate ([2 + 2] mechanism)[121–123] (Scheme 3).

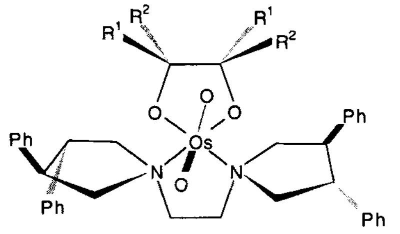
Although metallaoxetanes containing platinum, iridium, zirconium[121] or ruthenium[124] are known, no osmium metalaoxetane has ever been isolated and the NMR detection[125] of this four-membered intermediate is still controversial,[126] so the existence of a metallaoxetane intermediate remains hypothetical. Theoretical investigations[127] showed that the frontier orbitals of osmium tetraoxide are not directly set up for a [2 + 2] cycloaddition with an alkene but that nevertheless this mechanism could not be excluded. Furthermore both mechanisms can explain the strong acceleration by amines, owing to the distortion provoked by their complexation.[127]



[2]



Scheme 3



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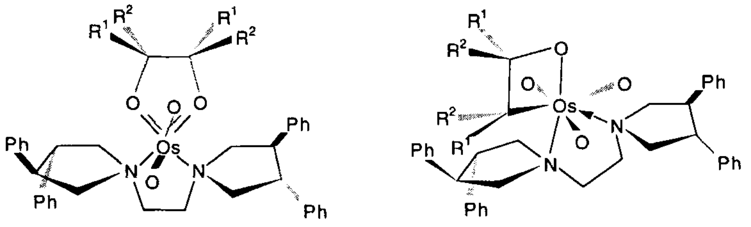


symmetrical [3+2] model **Tomioka model**

Figure 2 Hypothetical osmate–diamine complex transition states.

This continuing debate about the precise mechanism for ADH by OsO_4 particularly hinders the development of a useful model for predicting the transfer of chirality during the AD reaction catalyzed by diamines as well as by monoamines such as alkaloid derivatives.

2.2.3.1 Diamines

In 1986, Tokles and Snyder[100] concluded that it was impossible to choose between the two mechanisms for ADH on simple steric grounds. Later, Tomioka *et al.* proved that the enantioselectivity is not thermodynamically controlled by the stabilities of the different osmate–diamine complexes (ratio close to 1 with Tomioka's diamine) but is kinetically controlled by the relative stabilities of the diastereoisomeric transition states. They have characterized this osmate–diamine complex by X-ray crystallography as a hexacoordinated octahedral species **6** (Fig. 2).[102] The authors point out that a model with the symmetrical transition state of a [3 + 2] mechanism, resembling the osmate coordination, would predict based on steric grounds, the wrong stereoselectivity. They favored a [2 + 2] mechanism, which they claim explains the stereochemical outcome of the reaction.

In 1989, Corey *et al.* proposed a [3 + 2] model for ADH with OsO_4 and a diamine.[110] They suggested that a four-membered transition state as proposed by Tomioka would suffer prohibitive steric repulsions and that a symmetrical [3 + 2] model would predict the wrong stereochemistry. They proposed that a [3 + 2] cycloaddition occurs with one oxygen axial to the chelate ring and the other equatorial; the equatorial oxygen should be electron-rich (electron donation from N to the σ^*-orbital of *trans*-Os–O) relative to axial oxygen. This model (Fig. 3) was further supported by frontier orbital calculations.[128,129] According to the authors, this model can predict not only the stereochemical outcome of the ADH reaction with Corey's ligand, but also with those of Tomioka and Hirama.[101-109]

Recently MM2 calculations based on X-ray structures of OsO_4–amine complexes and osmate esters by Houk and co-workers[130] have suggested a symmetrical [3 + 2] mechanism.

2.2.3.2 Alkaloid monoamines

In spite of extensive structural and kinetic studies,[131-137] the mechanism of the Sharpless ADH reaction is still debated. Corey and Lohray agree to propose an [3 + 2] mechanism,[138,139] but Sharpless and co-workers by studying the temper-

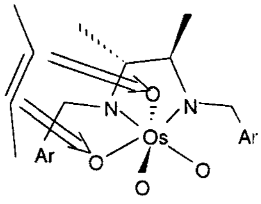
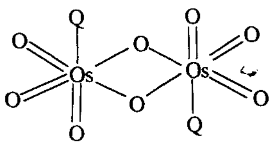


Figure 3 Corey model.

ature dependence of the enantioselectivities have shown that the reaction has at least two enantioselective steps differentially weighted according to temperature.[140] The authors think that if this is consistent with a stepwise [2 + 2] mechanism, it is incompatible with a concerted [3 + 2] mechanism with only one enantioselective step.

Corey and Lotto[138] have proposed the possibility of dimerization of OsO_4.Q (where Q is an alkaloid-based ligand) to afford **7**, which is supposed to be the reactive species. Only a small part of OsO_4.Q would need to dimerize if, as the authors suspected, the hexacoordinated osmium in the dimer is more reactive. Corey and Lotto proposed the structure **7**.



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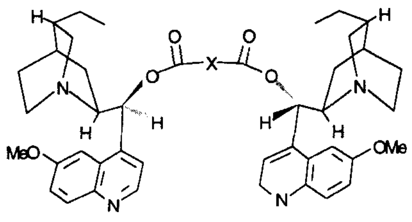
Lohray and Bhushan[139] have tested ligands of type **8** in ADH reactions. For X = $—C_6H_4—$, **8** is a very efficient ligand for ADH. This rules out structure **7**, which is not possible with **8** with such a rigid linkage. Lohray and Bhushan concluded that a dimeric $O_3Os[O_2]OsO_3$ is not possible and proposed that the reaction occurs on an OsO_4.Q complex. They supposed that the alkene is held over the π-cloud of the ligand (CO for acyl derivatives, aromatic ring for aromatic ethers) during the approach of the OsO_4 fragment. The differences between the steric requirements of the two faces of the alkene supposedly explain the observed enantioselectivity of the system.



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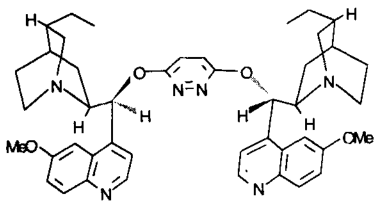
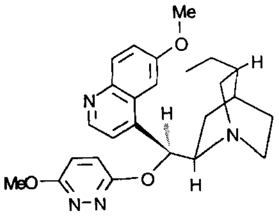
Corey *et al.* studied the ADH reaction for **9**, which has a 3,6-pyradazine bridge.[141] They were able to crystallize a (**9**)–$(OsO_4)_2$ complex. The X-ray analysis of this complex shows no bridging oxo-ligand but two OsO_4 units bound on each of the quinuclidine nitrogen atoms. The two osmium atoms are relatively close, leading the authors to propose a dimerization equilibrium they supposed to be obtained with a modest change of geometry.



9

Furthermore, comparison of the reactions of *o*-(trifluoromethyl)styrene with **9** and **10** shows that the enantiomeric ratio of the diol decreases from 65 to 2.3 when **9** is replaced by **10**, and that the rate is approximately 100-fold greater with **10**. Moreover, changing the concentration of reactants from 0.028 M to 0.00056 M causes the enantiomeric excess to drop from 97.4% to 84.4%. This decrease is not due to competing free osmium tetraoxide, as determined by a control experiment. The authors rationalized these observations by proposing two competing processes, one of high enantioselectivity involving a bridged dimer, and the other of a smaller enantioselectivity involving a monomeric complex.



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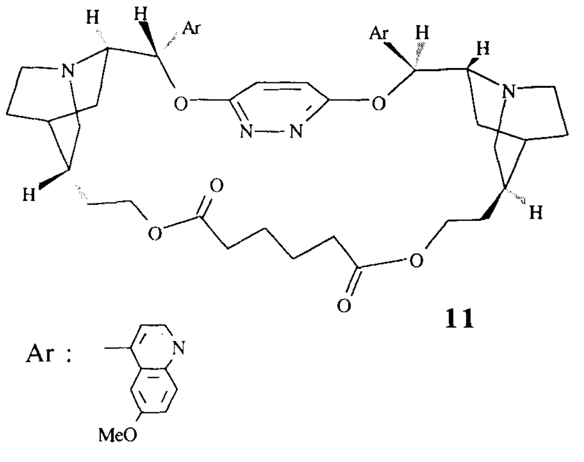
Recently, Corey and Noe[142] tested a new ligand (**11**), a rigid analog of **9** which does not allow dimerization to occur. Catalytic rates and enantioselectivities are essentially the same with **9** and **11**, so a mechanism requiring the complexation of both quinuclidine nitrogens, like the one via a μ-oxo-bridged bis-Os(VIII) complex, can be ruled out. This point has been confirmed by a kinetic study by Sharpless and co-workers[143] which shows a rate law which is first-order in OsO_4. This rate law contradicts a mechanism proceeding via a dimer, which is proved not to be the major compound in solution.

Finally, Sharpless and co-workers[144] carried out Density Functional Theory calculations on ruthe-



11

nium tetraoxide analogs which give the same enantioselectivity as the osmium tetraoxide complex with alkaloid ligands. This theoretical investigation shows that some metalloxetanes are energetically accessible and can be involved in the mechanism of ADH. Furthermore, a careful study of the relationship between the different structural parameters of the alkaloid ligand and binding constants on OsO_4, saturation rate constants and enantioselectivities is, according the authors, consistent with the [2+2] mechanism and has led them to propose a positive π-interaction between aromatic substituent on the alkene and the aromatic substituent on the oxygen of the alkaloid.[145]

2.3 Asymmetric epoxidation

The tremendous synthetic interest of an efficient access to chiral epoxides can easily explain the numerous efforts devoted to the most important method for producing chiral epoxides, the asymmetric epoxidation of prochiral alkenes.[146, 147]

2.3.1 Allylic alcohols epoxidation

2.3.1.1 First results

Different methods for asymmetric epoxidation of allylic alcohols have been designed by modifying the now classical method for achiral epoxidation, using an alkyl hydroperoxide and a metallic catalyst (Halcon process, etc.). The modifications involve introducing a chiral ligand in the coordination sphere of the metal. This approach was particularly efficient for the asymmetric epoxidation of allylic alcohols because the hydroxyl group of the allylic alcohol allows coordination of the allylic substrate on the metal, and the improved interaction between catalyst and substrate gives a better transfer of chirality.

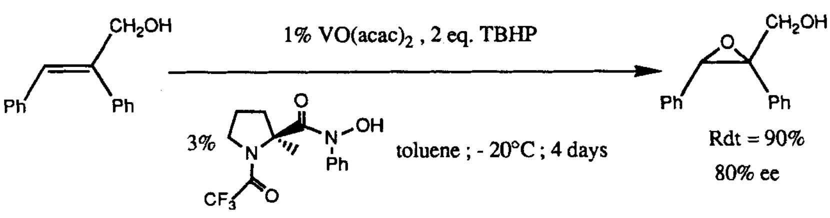
The first significant results were obtained with systems comprising an organic hydroperoxide and a catalyst with vanadium,[148, 149] molybdenum[150, 151] or aluminum.[152] The enantiomeric excesses are as high as 80% (V), 38% (Al) and 50% (Mo). The highest enantioselectivity is observed with a proline derivative as chiral inducer (Eqn [3]).[105] However, this asymmetric epoxidation system is not general: the enantioselectivities depend strongly on the nature of the alkenic substrate.

2.3.1.2 Sharpless' reagent

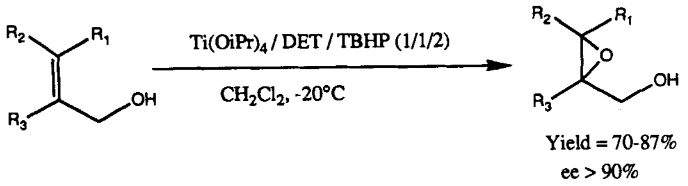
In 1980, Sharpless *et al.* described the first truly efficient method for an asymmetric epoxidation of allylic alcohols.[153, 154] Sharpless' reagent is a mixture of titanium isopropylate (1 eq.), diethyl tartrate (DET, 2 eq.) and t-butyl hydroperoxide (TBHP, 2 eq.). This reagent epoxidizes a number of allylic alcohols into the corresponding epoxy alcohols with good yields (70–90%) and with very good enantiomeric excesses (often over 90%)[153, 155] according to Eqn [4].

Sharpless' reagent, which is made from cheap, commercially available chemicals, combines many advantages:

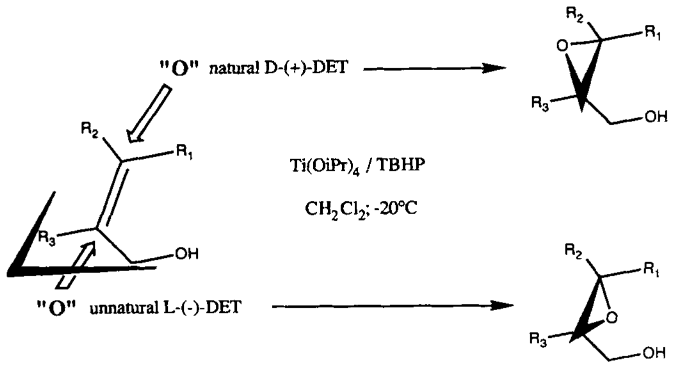
1. Enantioselectivities are high for a very large range of allylic alcohols (the ee of the epoxy alcohol produced is under 75% only for very sterically hindered allylic alcohols;[156] for example, 3-t-butyl-2,3-epoxypropanol is produced with 25% ee).
2. The absolute configuration of the epoxide produced can be predicted. Furthermore both enantiomers can be synthesized by



[3]



[4]

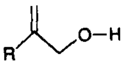


Scheme 4

choosing one or the other enantiomer of DET (Scheme 4).

(3) the system has excellent chemoselectivity: isolated carbon–carbon double bonds are unaffected, as illustrated by the example in Eqn [5].

(4) Less catalyst (5–10%) is required to perform the reaction in the presence of 3–4 Å molecular sieves.[157, 158] This decrease of the amount of catalyst is of particular interest for sensitive substrates like **12** because the use of smaller amounts of titanium limits epoxide-opening side reactions.[153]



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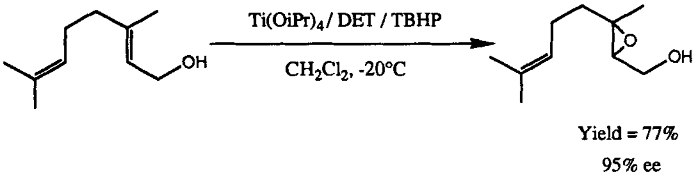
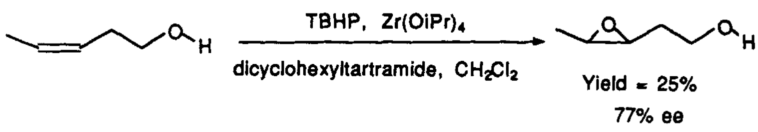
A number of ligands have been tested in the asymmetric epoxidation reaction with alkyl hydroperoxide catalyzed by titanium complexes,[158–160] but the best enantioselectivities are actually obtained with the original ligands, the tartrates. The ester moiety of the tartrate has little influence on the performance of the system if this ester part is not too bulky. For example, the use of (2,4-dimethyl)-3-pentyltartrate results in slow reactions and very low selectivities.[158] Furthermore, titanium isopropylate can be replaced by titanium t-butylate.[161] For some epoxy alcohols sensitive to epoxide opening by a nucleophile, the use of sterically hindered Ti(OtBu)$_4$ allows the limitation of this side reaction. Replacing Ti(OiPr)$_4$ by TiCl$_2$(OiPr)$_2$ affords the chlorodiols corresponding to the opening of epoxides by chloride ion, with an opposite enantioselectivity to those produced in the classical procedure.[162]

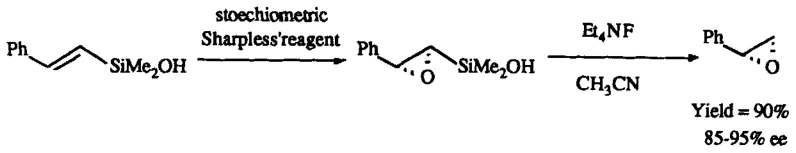
The Sharpless asymmetric epoxidation system has been applied to the epoxidation of homoallylic alcohols.[163] The enantioselectivity is opposite to those observed for allylic alcohols but the enantiomeric excesses are lower (23–55%). Replacement of titanium by zirconium much increases the performance (Eqn [6]).[164]



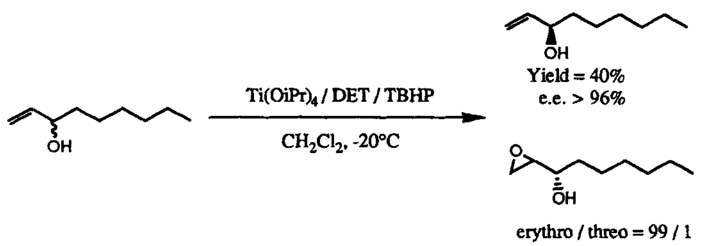
[5]



[6]



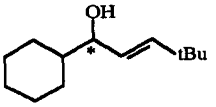
[7]



[8]

The reagent was also applied recently to alkenylsilanols (Eqn [7]).[165]

The Sharpless method can be applied successfully to kinetic resolution of chiral allylic alcohols. Secondary allylic alcohols with an asymmetric carbon bearing the hydroxyl group can be resolved very efficiently (ee often over 95% with 35–45% yield),[158,166–172] as illustrated by Eqn [8]. The ratios k_f/k_s are particularly high for this reaction (e.g. as high as 300 for **13**).



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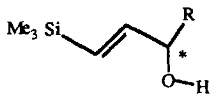
It is noteworthy that the kinetic resolution is particularly efficient for silylated secondary allylic alcohols and especially for those like **14**, which exhibit a k_f/k_s of over 1000![173]



14

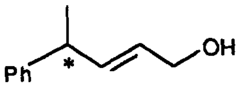
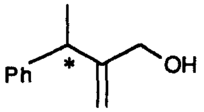
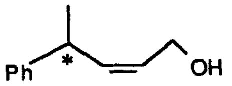
Some interesting results are also obtained for primary allylic alcohols bearing a lateral chain with an asymmetric carbon,[174] but this method is not general, as illustrated by Table 4.

The method was also applied other substrates related to allylic alcohol, e.g. β-hydroxyamines,[175–177] β-hydroxysulfides,[174] allenyl alcohols,[174] α-acetylenic carbinol,[174] α-furyl carbinols,[178, 179] α-furfuryl amides[180] and alkenylsilanol.[181]

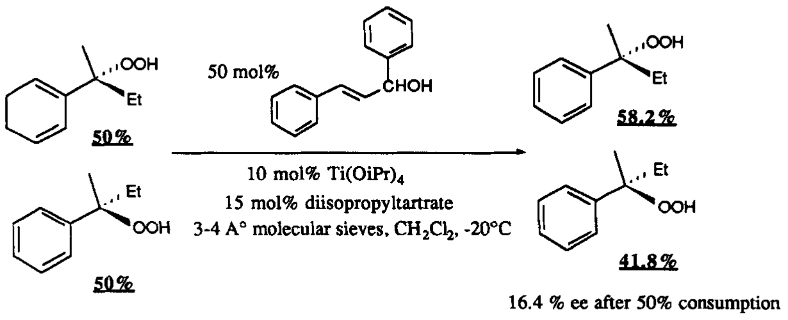
Recently, the Sharpless asymmetric epoxidation method has been applied to the kinetic resolution of chiral alkyl hydroperoxide.[182] (Eqn [9]).

The enormous synthetic interest of the Sharpless reagent prompted the development of a heterogeneous version of the system. In 1983,

Table 4 Kinetic resolution of allylic alcohols using the Sharpless reagent

Alcohol	ee[a] (%)
	6
	>95
	80

[a] For 60% conversion



[9]

Farall *et al.* described a system in which the tartaric esters were immobilized on 1% cross-linked polystyrene resins via CH_2OH (polymer A) or CH_2CH_2OH groups (polymer B)[183] (Fig. 4).

An enantiomeric excess of 66% can be obtained in the epoxidation of geraniol using polymer B. This interesting level of enantioselectivity is, however, significantly lower than those obtained in the homogeneous version (95% ee).[158] Polymer B is a much better ligand for the reaction than polymer A, probably because the link between the polymeric moiety and the active tartrate is longer, so the steric hindrance is reduced. By further increasing the size of the link it may be possible to bring the selectivity up to a useful range.

Another interesting attempt at a heterogeneous version of Sharpless reagent was described in 1990 by Choudary *et al.*[184] The new source of titanium in this system is a clay in which the Na^+ ion has been replaced by titanium(IV) ions; a Ti(IV) montmorillonite called Ti-PILC is used instead of $Ti(OiPr)_4$. The new system is catalytic in titanium (3%) without use of 3–4 Å molecular sieves. Yields and enantiomeric excesses are very close to those obtained with the catalytic Sharpless system. Furthermore, the concentrations can be increased, because Ti-PILC is a poor catalyst for the side reactions of epoxide-opening of the epoxy alcohol.

Recently it was shown that an addition of calcium hydride (5–10 mol %) and silica gel (10–15 mol %) to Sharpless' reagent speeds up the reaction without changing the yields and enantioselectivities much,[185, 186] as illustrated by the example in Scheme 5.

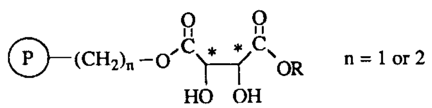
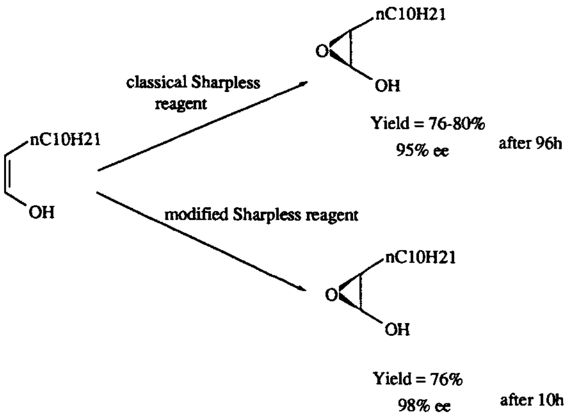
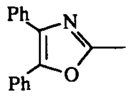


Figure 4 Heterogeneous version of Sharpless reagent: representation of polymers A ($n = 1$) and B ($n = 2$)



Scheme 5

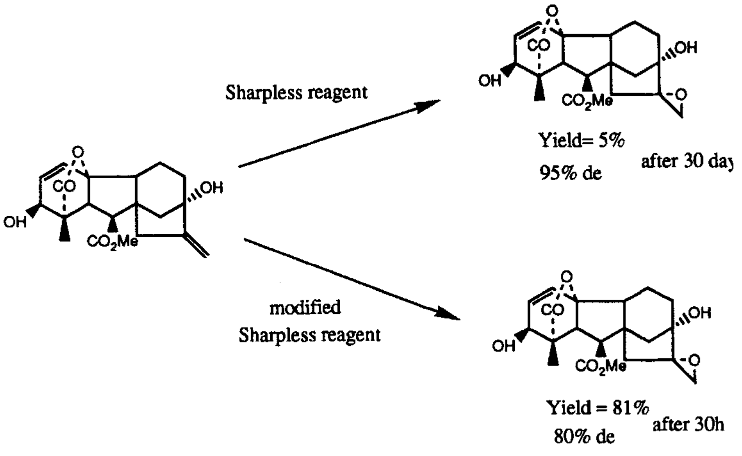
This system can be especially useful for substrates incompatible with the Sharpless conditions. For example, allylic alcohols bearing an ester group can be epoxidized directly by the modified Sharpless' reagent. With the classical Sharpless' reagent, a protection of the ester group by a diphenyloxazole group is necessary.[187] This is well illustrated by the case of methylgibberelate[188] (Scheme 6).



diphenyloxazole

Recently a system was described for asymmetric epoxidation of allylic alcohols using amino-acid derivative–$Ti(OiPr)_4$ as catalyst with 1,1-diphenylethyl hydroperoxide.[189]

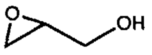
Synthetic aspects. Although the Sharpless system for asymmetric epoxidation is essentially



Scheme 6

limited to allylic and, to a lesser extent, homoallylic alcohols, it has enjoyed widespread use since the mid-1980s. In fact, the availability of numerous enantiomerically enriched epoxy alcohols gives access to many molecules in an almost enantiomerically pure form, as exemplified in Schemes 7 and 8.

The enormous synthetic utility of epoxy alcohols as intermediates has made the Sharpless reaction one of the most-used methods in asymmetric synthesis. More than 300 publications in the last ten years have described the use of this method for the preparation of many chemicals, especially sugars, terpenes, leucotrienes, pheromones, antibiotics, etc.[190–192]



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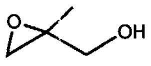
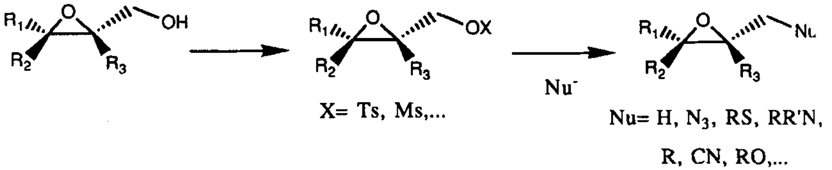
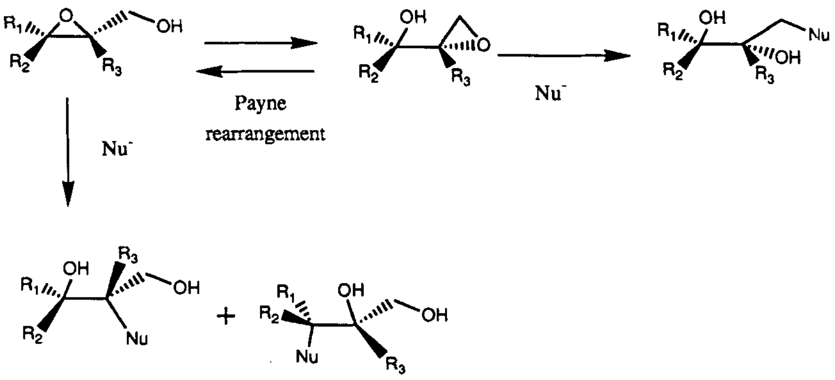


16

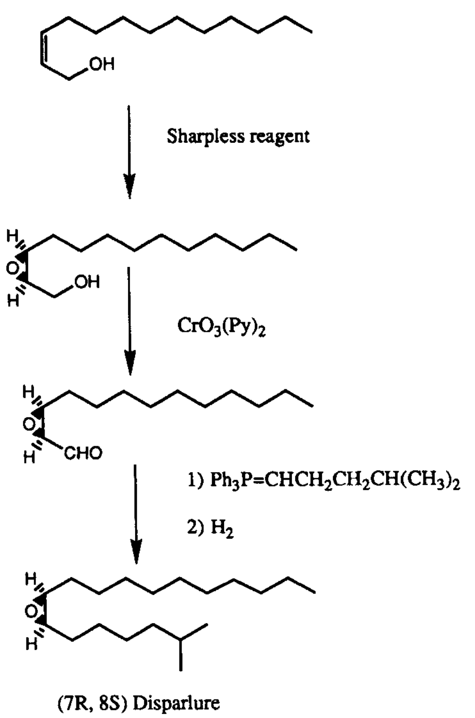
The Sharpless asymmetric epoxidation reaction is used industrially by ARCO Chemical Company to produce the glycidols **15** and **16** and by J. T.



Scheme 7



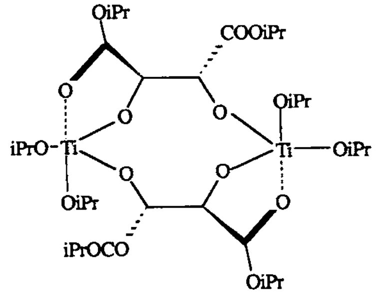
Scheme 8



Scheme 9 Synthesis of (7*R*,8*S*)-disparlure.

Baker to produce several kilograms of (7*R*,8*S*)-disparlure (Scheme 9).[193]

Mechanistic aspects. In dichloromethane solution with concentrations similar to those of the Sharpless system, vapor-phase osmometry methods indicate a species of average molecular weight 760 ± 20, corresponding to dimeric $Ti_2(OiPr)_4(tartrate)_2$.[194, 195] The first structure proposed for this dimer was a ten-membered ring (**17**),[194] but X-ray analysis of related complexes like $Ti_2(OiPr)_4(tartramide)_2$[196, 197] in which two monomeric units $Ti(OiPr)_2(tartramide)$ are bound by bridging tartramide oxygen prompted Sharpless and co-workers to propose for this dimer the structure **18**.[195] IR, UV, ^1H, ^{13}C and ^{17}O NMR spectra are consistent the hypothesis of the dimer (**18**) as the major product in solution,[195] but, so far, no X-ray structural determination for $Ti_2(OiPr)_4(tartrate)_2$ has been performed.



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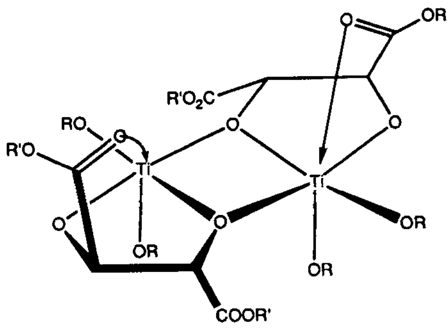
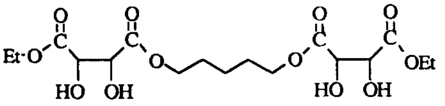


18

Recently, based on results of a careful NMR study of $Ti_2(OiPr)_4(tartrate)_2$–amine complexes, Potvin and Bianchet proposed the structure **17** as the most probable for this complex.[198]

Sharpless and co-workers favor a dimer as the major catalyst, as suggested by the kinetics of the epoxidation reaction which are first-order in dimer, as well as by the fact that IR and ^1H NMR spectra do not change when the catalyst concentration is decreased by a factor of 10.[199, 200] It is possible, though improbable, that the active catalyst could be not the dimer but a minor species which is at such low concentration that it is not detectable by spectroscopy and which exhibits an apparent first-order kinetics in catalyst. The fact that a linked bis-tartrate such as **19** can replace 2 eq. of DET almost without changing the selectivity of the reaction provides further support for the involvement of the dimer as catalyst.[201]



19

The rate law of the Sharpless asymmetric epoxidation reaction is given by Eqn [10].

$$\text{rate} = k\,\frac{[\mathrm{TBHP}][\mathrm{Ti_2(OiPr)_4(tartrate)_2}][\text{allylic alcohol}]}{[\mathrm{iPrOH}]^2} \qquad [10]$$

This kinetic law is in full agreement with a mechanism in which the rate-determining step would be ligand exchange on dimeric $Ti_2(OiPr)_4(tartrate)_2$ to give **20** (Eqn [11]), which quickly collapses to give the epoxy alcohol:

$$Ti_2(OiPr)_4(tartrate)_2 + TBHP + allyl\ alcohol \rightleftharpoons Ti_2(OiPr)_4(tartrate)_2(OOtBu)(O\text{-}allyl) + 2iPrOH \quad [11]$$

(20)

Sharpless *et al.* proposed the structure shown in Fig. 5(a) **20**. The view along Ti–O(I) bond axis is represented in Fig. 5(b).

The oxygen atom transfer step is supposedly a nucleophilic substitution S_N2 on O(I) by the alkene group parallel to the O(I)–O(II) bond axis. Based on simple steric arguments, the steric requirements of the intermediate (**20**) allow the prediction of which enantiomer of a chiral allylic alcohol would react more quickly during a kinetic resolution. However, the enantioselectivity of this reaction is hard to explain. The enantiofacial selectivity corresponds to a spiro approach of the carbon–carbon double bond towards peroxidic oxygen in intermediate **20**.

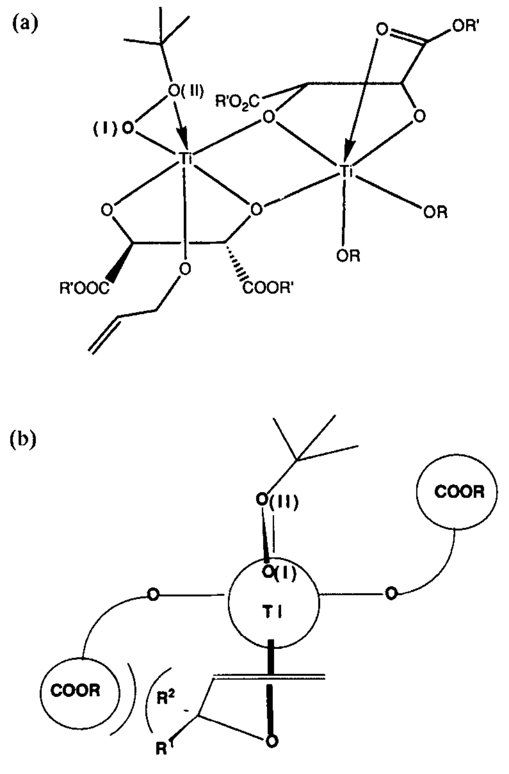
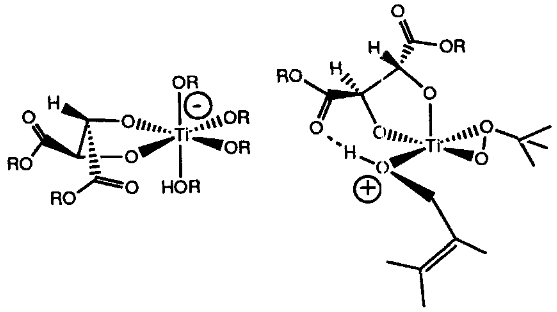


Figure 5 (a) Structure proposed by Sharples *et al.* for **20**. (b) View along Ti–O(I) bond axis.

Other mechanistic proposals that have been made include the participation of an intermediate orthoester[199] or, more recently, catalysis involving an ion pair (**21**).[202] Frontier orbital calculations support the Sharpless proposal but cannot rule out other hypotheses.[129, 203, 204]



(21)

2.3.2. Isolated alkene epoxidation

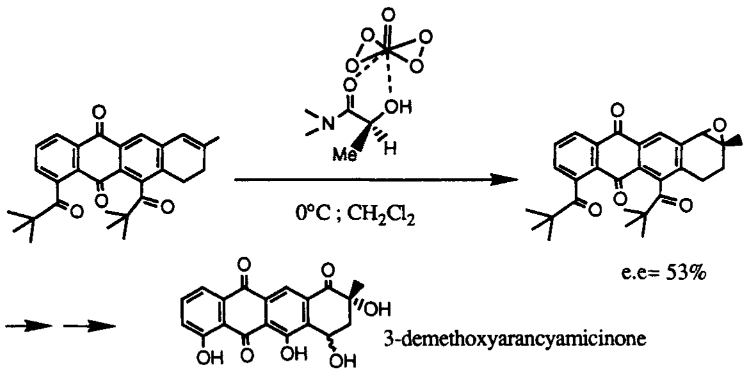
While 1,2-epoxy alcohols can be obtained easily in an enantiomerically pure form using Sharpless' reagent, no such versatile method exists for the asymmetric epoxidation of unfunctionalized alkenes. Significant progress has been made in this area nonetheless.

2.3.2.1. Epoxidation reactions with a stoichiometric chiral inducer

In 1979, chiral oxo-peroxo-molybdenum(VI) complexes were reported to epoxidize isolated alkenes with moderate enantioselectivities (15–35% ee).[205] The chiral ligands used were lactamides. X-ray analysis shows that these complexes have slightly distorted pentagonal-bipyramidal geometry.[206] The best enantioselectivity was found for the synthesis of a tetracyclic anthracyclinone, 3-demethoxyaranciamycinone[207] (Scheme 10).

The enantiomeric excess is roughly constant during the course of this reaction; this indicates that the enantiomeric enrichment is due to the enantioselectivity of the epoxidation reaction and not to a kinetic resolution in the reaction medium of the epoxide formed.[208]

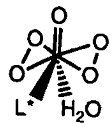
In the presence of the enantiomerically pure diols, epoxides can be obtained with excellent enantiomeric excesses (up to 95%). The stereochemical outcome depends only on the nature of



Scheme 10

the diol, because the epoxide produced is kinetically resolved by a molybdenum–diol complex.[208]

The catalytic activity of some molybdenum complexes (**22**) with chiral monodentate ligands have also been tested; the observed enantioselectivities are low (0.7–8.5% ee).[209]



22

2.3.2.2. Epoxidation reactions with a chiral catalyst

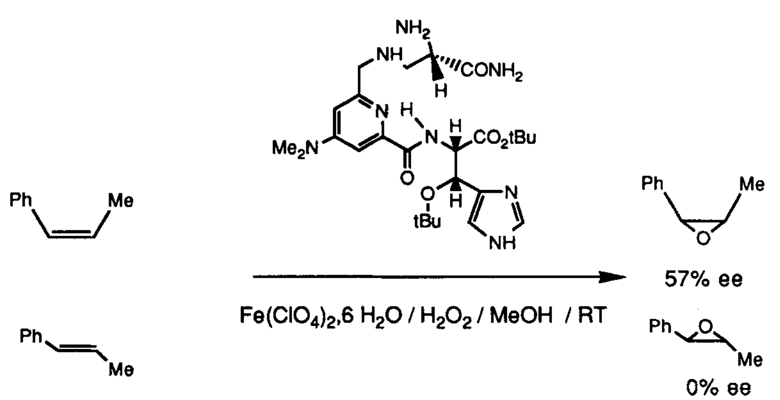
The first report of the use application of a chiral catalyst for epoxidation reactions described the use of a chiral molybdenum(VI) complex with diol ligands as catalyst for the asymmetric epoxidation of unfunctionalized alkenes.[210] The results are disappointing: yields (25–77%) and enantiomeric excesses (0.7–14%) are low. Some cobalt(III) complexes have also been used in the epoxidation of styrenes by iodosylbenzene with good yields but low enantioselectivities (0–17%).[211] Some sterically hindered chiral titanocenes with t-butyl hydroperoxide as oxidant (2–22% ee),[212,213] as well as ruthenium(III)–pyridyloxazolines with sodium periodate as oxidant,[214] have been used.

More interesting is the system described by Strukul and co-workers using platinum(II) complexes with chiral diphosphines.[215] The cationic complex $[(\text{chiraphos})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)],\text{BF}_4$ used in dichloromethane with H_2O_2 catalyzes the epoxidation of molecules as tiny as propene to the corresponding epoxide with 42% ee!

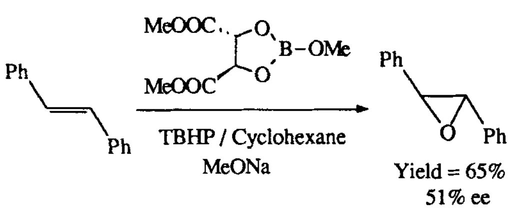
A biomimetic model of the bleomycin–iron(II) complex can epoxidize *trans*-alkenes with a significant level of enantioselectivity while the corresponding *cis*-alkenes give a racemic mixture using this catalyst[216,217] (Eqn [12]).

Recently the use of a chiral peroxidic boron complex for asymmetric epoxidation of isolated olefins was reported[218,219] (Eqn [13]).

The metallic (iron or manganese) complexes of chiral porphyrins constitute a family of catalysts for asymmetric epoxidation of unfunctionalized



[12]

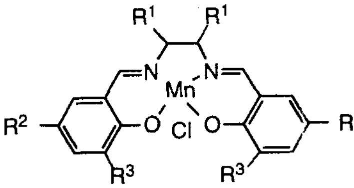


[13]

alkenes of particular interest.[220] High enantioselectivities and good catalytic activity can be obtained, but the selectivities are strongly dependent on the substrate structure and cannot be easily predicted. For this reason, and owing to the difficult synthesis of chiral porphyrins, the porphyrin-based systems do not appear to be of great synthetic interest. Since the first reports of Groves and co-workers,[221] numerous porphyrinic systems for asymmetric epoxidation have been described by the groups of Mansuy (12–51% ee),[222] Kodadek (20–40% ee),[223] Groves (20–72% ee),[9] Naruta and Maruyama (54–96% ee),[224–228] Halterman (41–76% ee),[229] Momenteau (0–33% ee),[230] Colleman (21–88% ee),[231,232] Inoue (42–58% ee),[233] Hevesi (10–16% ee),[234] Marchon and Scheidt,[235] etc.

In 1990, Jacobsen and co-workers described a very efficient system for asymmetric epoxidation of isolated alkenes using a chiral salen–manganese(III) complex and iodosylmesitylene.[236] The enantioselectivities are especially high for aromatic *cis*-1,2-disubstituted alkenes (Eqn [14]).

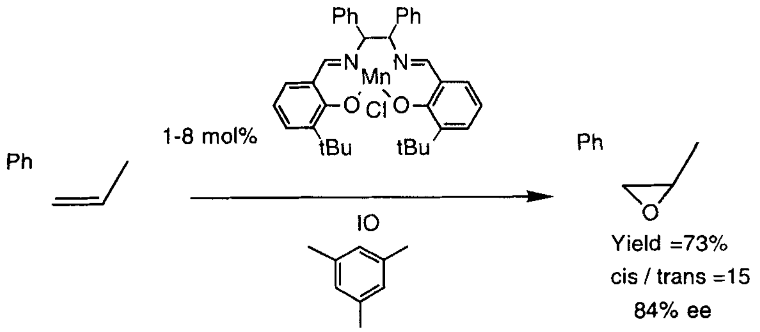
However, the enantioselectivities are much lower for *trans*-disubstituted alkenes (33% ee for t-stilbene) or *gem*-disubstituted alkenes (30% ee for α-methylstyrene). Moreover, a significant proportion of *anti* epoxidation product is observed (3–20% for *cis*-1,2-disubstituted alkenes in conjugation with an aryl group).[237]



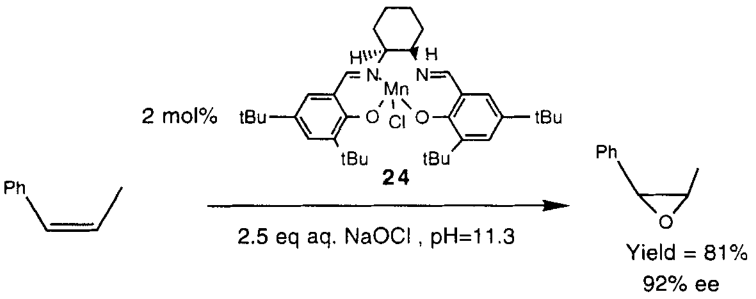
23

By modifying the groups R^1, R^2, R^3 in complex **23**, Jacobsen and co-workers were able to increase slightly the performance of the system. They also found that it is possible to use bleach instead of iodosylmesitylene[238,239] as oxidant. H_2O_2 can be used also but the enantioselectivity drops (from 92% ee to 52% ee for 1,2-dihydronaphthalene).[240] The best results are obtained with complex **24** (Eqn [15]).

The Jacobsen system was applied with particu-



[14]



[15]

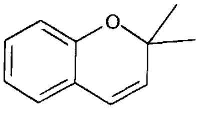
lar success to chromens,[241] dienes[242] and enynes.[243] It was also applied to the taxol side chain synthesis.[244]

A few months after Jacobsen's first report, Katsuki described a related system of asymmetric epoxidation. The main difference is that the R^3 group in **23** is not a tertiary alkyl group (typically tBu) as in the Jacobsen system but a chiral secondary alkyl group.[245] By modifying R^1, R^2, R^3 also, the authors produced a new set of interesting chiral salen complexes,[246–252] but the enantioselectivities observed with these complexes are often lower than with Jacobsen ligands. Moreover, Katsuki and co-workers found that donor ligands can improve the enantioselectivities of the system.[253]

Some related systems were reported, with R^3 = silyl (18–53% ee),[254] with $R^3 = R^2 = Cl$ or Br (10% ee),[255] with a ligand bearing an axial donor group (ee up to 64%),[256] with an α-alkoxycarbonyl-β-ketoiminate ligand instead of salen (33–84% ee),[257] and with some salen–ruthenium catalysts [50–80% ee but with low conversions to epoxide (10–40%)].[258] Mukaiyama and co-workers described the use of dioxygen in presence of pivalaldehyde as oxidant with Jacobsen ligands: yields and enantioselectivities (60–77% ee) were good but significantly lower than in the original version.[259]

A mechanistic study with the use of **25** as a probe showed that the manganese(III)–salen-mediated expoxidation of unfunctionalized alkyl-substituted alkenes is a concerted process[237] because no products of cyclopropyl ring-opening were observed (see Scheme 11). In contrary, the amount of *trans*-epoxides obtained from conjugated *cis*-alkenes suggest a stepwise mechanism involving a radical intermediate for this substrate.[260]

For **23** with $R^1 = Ph$ and $R^3 = tBu$, variation of the R^2 group (from OMe to NO_2) shows that log(ratio of enantiomers) varies linearly with the Hammett coefficients of the R^2 groups.[261] The best enantiomeric excesses are obtained with electron-donating groups and the effect can be very important: for **26**, 22% with $R^2 = NO_2$ but 96% for R = OMe!



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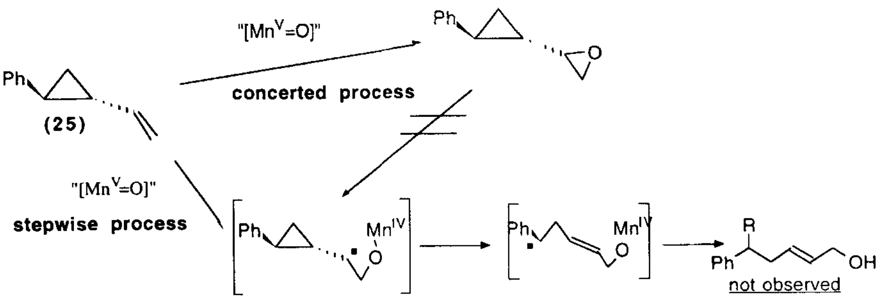
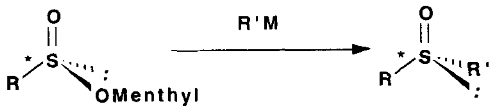
The authors explain the favorable effect of electron-donating groups not by a change in conformation or in metal–oxo bond length but by a more product-like transition state, resulting in smaller separation between substrate and catalyst and so better steric differentiation. The sense and degree of enantioselectivity can be easily explained on steric grounds, using the hypothesis of side-on approach.[236] A precise study by ligand modification supports this hypothesis and suggests an approach along the nitrogen–metal axis.[262]

3 ASYMMETRIC OXYGEN ATOM TRANSFER ON HETEROATOMS: OXIDATION OF SULFIDES

There is a great need for efficient methods to obtain chiral sulfoxides, which are very valuable intermediates in organic synthesis.[263] The most popular synthesis of chiral sulfoxides is by the Andersen reaction of an organometallic reagent with a chiral menthyl p-tolylsulfinate[264, 265] (see Eqn [16]) (the two enantiomers of menthyl p-tolylsulfinate are commercially available). But the Andersen method is limited to the synthesis of sulfoxides of type RS(O)Ar, so other convenient



Scheme 11



[16]

means of access to chiral sulfoxides are still welcome. One solution is asymmetric sulfide oxidation to sulfoxides, which becomes increasingly attractive as it is improved.[8]

3.1 Sulfide oxidation reactions with a stoichiometric chiral inducer

In 1984, Pitchen and Kagan reported that a modified Sharpless' reagent obtained by changing the ratio Ti(OiPr)$_4$/tartrate from 1:1 to 1:2 and adding 1 eq. of water is a stoichiometric epoxidizing reagent for asymmetric oxidation of sulfides.[266] This new system can epoxidize with good enantioselectivities a large range of aryl alkyl sulfides (20–98% ee) and dialkyl sulfides (50–71% ee),[267, 268] vinyl sulfides (2–95% ee),[240, 269] disulfides to thiosulfinates,[270, 271] sulfenamides to sulfinamides,[244] sulfenates to sulfinates,[245] and 1,3-dithianes (0–98% ee).[272, 273] In every case, both sulfoxide enantiomers can be synthesized because the two tartrate enantiomers are commercially available. The use of cumene hydroperoxide instead of t-butyl hydroperoxide, in contrast to trityl hydroperoxide, increases the enantiomeric excess of the sulfoxide produced[274, 275] (for *p*-tolyl-SMe, 96% ee with cumene hydroperoxide, 16.3% ee for trityl hydroperoxide, 89% ee for t-butyl hydroperoxide). Moreover, the use of cumene hydroperoxide makes it possible to decrease the concentration of titanium complex to a catalytic amount (0.25 mol %).[248, 249]

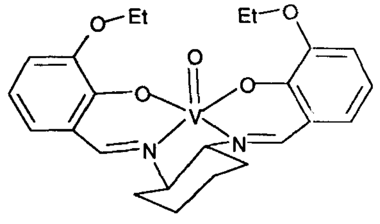
The system was recently applied successfully to the kinetic resolution of a chiral thiazolidinone biologically active as antioxidant.[276] Moreover, Rhône-Poulenc Rorer Ltd recently applied Kagan's system to a large-scale asymmetric synthesis of a biologically active sulfoxide[277] (Eqn [17]).

MM2 calculations by Jørgensen[278] suggested a direct interaction of the sulfide with the peroxygen atom on the peroxotitanate but a precoordination of the sulfide to the titanium atom cannot be excluded.

Another modified Sharpless' reagent was described by Di Furia, Modena and co-workers with a Ti(OiPr)$_4$/tartrate ratio of 1:4, without adding water.[279–283] The enantioselectivities are often lower than with Kagan's reagent but can be higher, particularly for 1,3-dithianes.[284–286]

3.2 Sulfide oxidation reactions with a chiral catalyst

A number of metallic complexes were used as catalysts for asymmetric oxidation of sulfides to sulfoxides with various oxidants such as Δ-tris-(1,10-phenanthroline)nickel(II) on montmorillonite with NaIO$_4$ (0–78% ee)[287] or Δ-tris-(2,2′-bipyridyl)ruthenium(II) with O$_2$ and light (15–20% ee),[288] vanadium and molybdenum complexes with t-butyl hydroperoxide in chiral alcohols (0.6–9.8% ee),[289] salen–vanadium complexes such as **27** (4–40% ee) with cyclohexyl hydroperoxide,[290, 291] a salen–dimeric titanium complex (**28**) with trityl hydroperoxide (5–43% ee)[292] or t-butyl hydroperoxide



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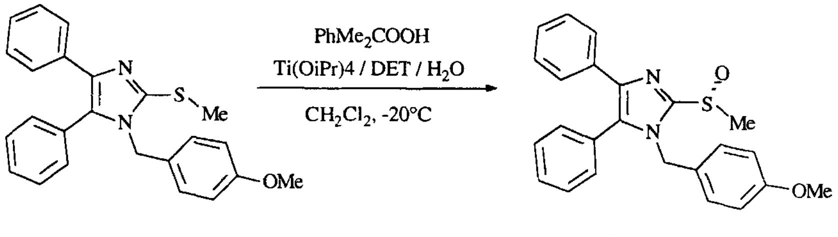
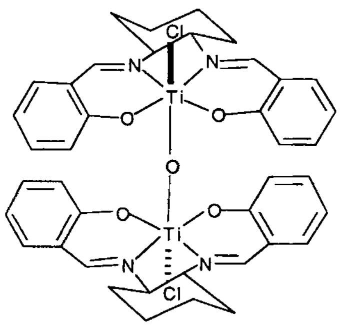


[17]

DET = diethyltartrate

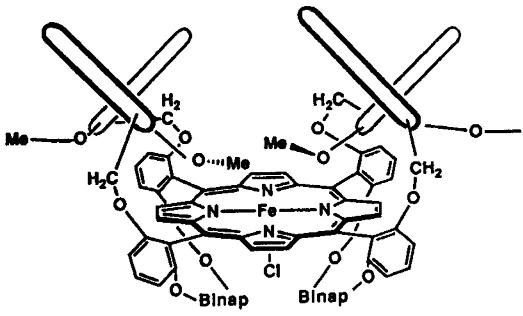
Yield = 71%
98-99% ee



28

(5–24% ee)[293,294] and vanadium-pillared montmorillonite with DET and t-butyl hydroperoxide (16–25% ee).[295] The salen–manganese(III) catalysts for alkene epoxidation were also tested in asymmetric oxidation of prochiral sulfides by Jacobsen (34–68% ee with H_2O_2 as oxidant)[296] and Katsuki (40–90% ee with PhIO as oxidant).[297]

Since the Naruta and Maruyama's first reports in 1991,[298,299] many porphyrin–iron or manganese complex-based systems for asymmetric oxidation of prochiral sulfides were reported by Groves (14–48% ee),[9] Halterman (40–68% ee),[300] Inoue (18–71% ee),[301] and Zhou *et al.* (5–15% ee).[302,303] The best results are obtained with a "twin coronets" porphyrin (**29**) with iodosylbenzene in the presence of 1-methylimidazole (23–73%).



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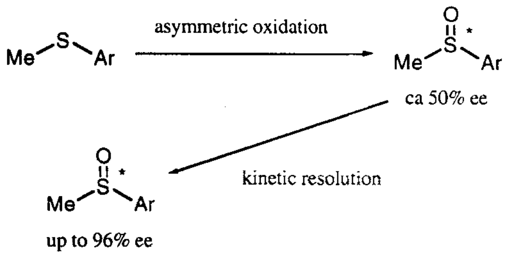
Using poly(amino-acid)-coated platinum electrodes, it is possible to oxidize sulfides to sulfoxides. The performance is quite different according to the substrate and the type of electrode but enantiomeric excesses up to 93% were observed for the oxidation of tert-butylphenylsulfide with a poly(L-valine)-coated electrode.[304,305]



Scheme 12 Asymmetric oxidation with $Ti(OiPr0_4$/ binaphthol.

Recently, however, Uemura and co-workers[306,307] described the combination of $Ti(OiPr)_4$ and binaphthol (ratio = 1:2). The highest enantioselectivities (up to 96% ee) were obtained with commercial aqueous 70% t-butyl hydroperoxide in CCl_4. Water is necessary to obtain an effective catalyst but also to maintain its properties. The enantiomeric excess changes during the course of the reaction. This fact is an indication of a further kinetic resolution of the sulfoxide formed (see Scheme 12), which was afterwards proved to occur by kinetic resolution of a partially resolved sulfoxide in the reaction conditions.

The different methods described in this section, if they can give good results, are not general, and rarely reach the range of enantioselectivity of synthetic usefulness (>90%).

Recently, Choudary *et al.* reported that titanium-pillared montmorillonite Ti-PILC1 (9 mol %) associated with DET (18 mol %) is a very efficient catalyst for asymmetric oxidation of sulfides with t-butyl hydroperoxide in dichloromethane (9–92% ee).[308] The enantioselectivities are especially good for sulfides of the alkyl-SMe type [75–80% ee, i.e. higher than with the Kagan reagent (54–71% for the same substrates)] and sulfides of the ArSMe type (81–92% ee). Moreover, the easier work-up by simple filtration and the possibility of reusing the catalyst make this new system especially attractive.

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