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Emerging applications of asymmetric dihydroxylation chemistry

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Abstract

Applications of recently discovered asymmetric dihydroxylation (ADH) of alkenes in synthetic organic chemistry have been described. ADH reaction has been successfully implemented in the synthesis of several natural products, drugs and drug intermediates. It has also been utilized in kinetic resolution and double diastereoselections in a few cases.

Key words: ADH, oxidation, unfunctionalized alkenes, diols.

1. Introduction

During 80s much attention was focussed on the asymmetric catalytic reactions[1]. Stereoselective oxidation is one of the major goals in organic chemistry. Discovery of Sharpless catalytic asymmetric epoxidation is a landmark in the oxidation chemistry, which utilizes allylic alcohols as substrates[2]. However, stereoselective oxidation of unfunctionalized olefins is a much tougher goal to achieve, especially in a catalytic fashion. In 1988, once again, a major breakthrough in the successful oxidation of unfunctionalized alkenes to diols was reported by Sharpless and co-workers[3]. Since the discovery of ADH reaction, a number of new chiral ligands and reaction conditions have been developed for the continuous improvement of enantioselective oxidation of alkenes(Chart 1). In 1992, we have compiled literature through 1991[4]; however, during the last two years, more emphasis has been laid on the application of this novel reaction. The present paper will cover literature up to November 1993 and this review should be treated as complementary to the previously published one[4].

2. Applications

2.1. Stereoselective syntheses of natural products

One of the earliest applications of asymmetric dihydroxylation strategy has been reported by Tomioka *et al*[5] for the synthesis of anthracycline antibiotics, though the reaction was carried out using stoichiometric amount of chiral auxiliary and osmium tetroxide. A very expeditious

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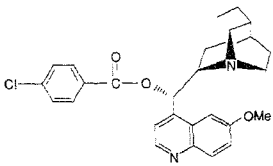
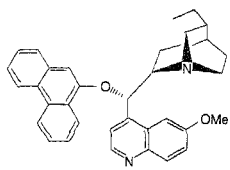
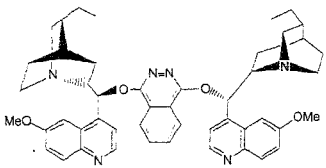


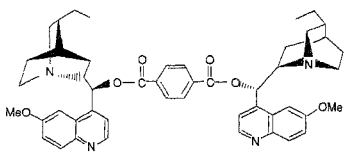
DHQD–CLB
Sharpless *et al*
J. Am. Chem. Soc., 1988



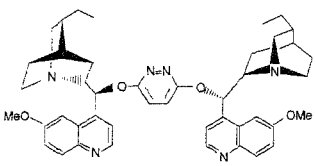
DHQD–PHN
Sharpless *et al*
J. Org. Chem., 1991



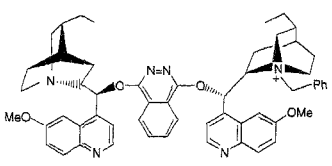
$DHQD_2$–PHAL
Sharpless *et al*
J. Org. Chem., 1992



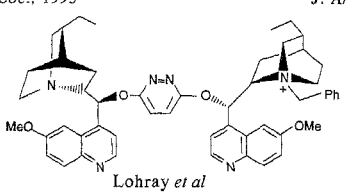
$DHQD_2$–TP
Lohray and Bhushan
Tetrahedron Lett., 1992



$DHQD_2$–PY
Corey *et al*
J. Am. Chem. Soc., 1993



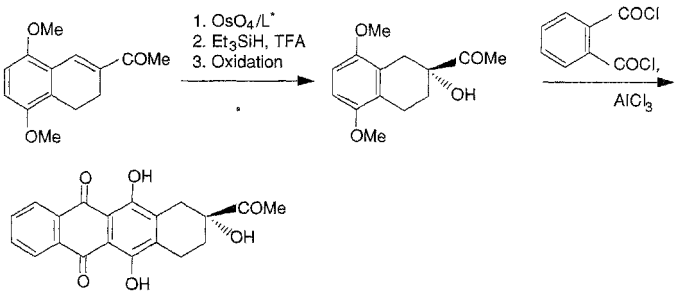
Sharpless *et al*
J. Am. Chem. Soc., 1993



Lohray *et al*
Unpublished results

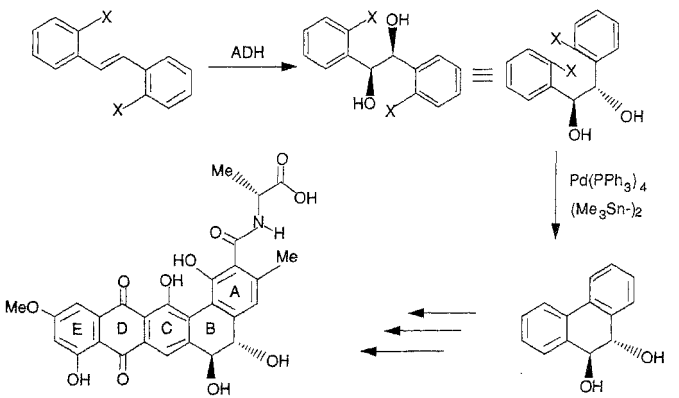
Chart 1.

synthesis of anthracycline was achieved using asymmetric dihydroxylation reaction as a key step to introduce the chirality in the molecule (Scheme 1).



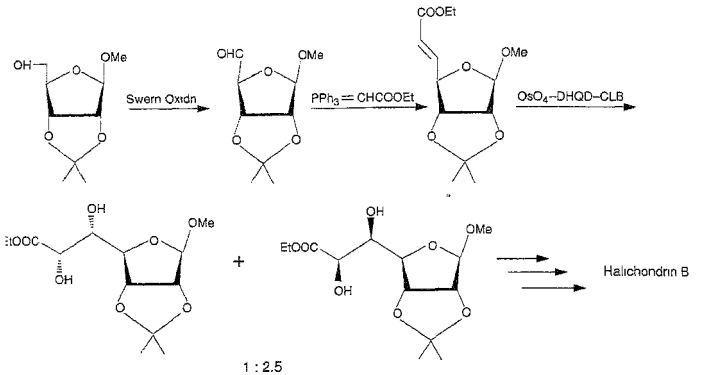
SCHEME 1.

Kelly and co-workers[6] have generated the B ring diol in the planned synthesis of pradimicinone *via* ADH reaction (Scheme 2).



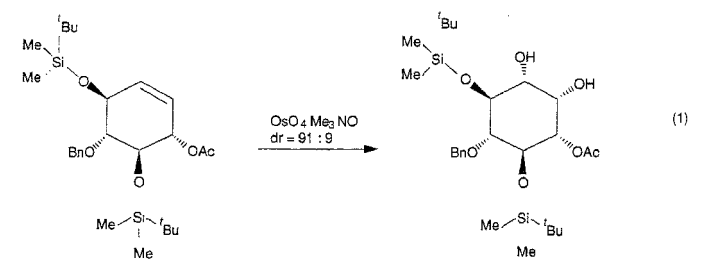
SCHEME 2. Pradimicinone

Cooper and Salomon[7] synthesized the pentacyclic intermediate from readily available ribofuranoside which is finally used in the synthesis of antitumor agent Halichondrin B (Scheme 3).



SCHEME 3.

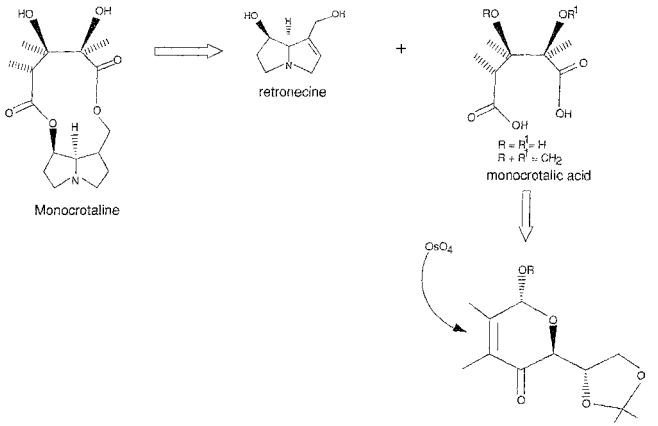
An inverse approach to achieve diastereoselective dihydroxylation was carried out by Arjona *et al*[8] by using chiral substrates and osmium tetroxide with NMO as co-oxidant. They have prepared *myo*-inositols from Conduritol B acetate using dihydroxylation as the key step (eqn 1).



(1)

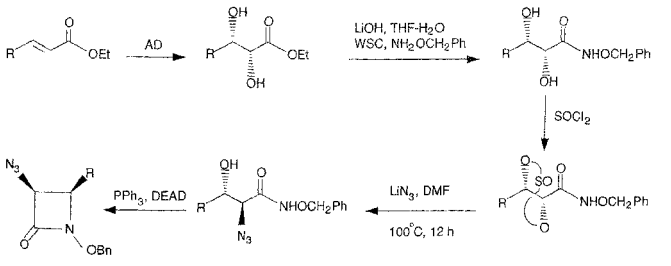
Myo-inositol has been a useful synthetic target due to well-documented biological activities of its derivatives[9]. Similar approach has been adopted by Honda and co-workers[10] to synthesize monocrotaline, a natural product, which is a 11-membered alkaloid.

The macrocyclic lactone is made up of two parts, necine base, retronecine and monocrotalic acid (Scheme 4). Monocrotalic acid was synthesized by dihydroxylation of chiral pyrones.



SCHEME 4.

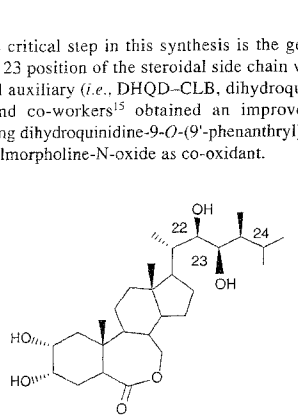
Similarly, Ireland *et al*[11] have prepared chiral epoxide *via* diol prepared by Sharpless asymmetric dihydroxylation method. The epoxide was finally used in the synthesis of FK-506. Ikemoto and Schreiber[12] used ADH method for preparing polyols from the corresponding olefins in the synthesis of Hikizimycin, an antihelmintic agent. Kim and Sharpless[13] prepared β-lactams from 2,3-dihydroxyesters *via* cyclic sulfites (Scheme 5).



SCHEME 5.

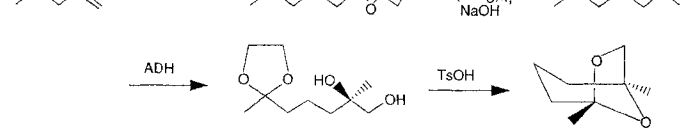
Zhou and co-workers[14] have examined several substrates under ADH conditions for the synthesis of the plant growth regulators, brassinolide and its analogues, such as homobrassinolide,

epibrassinolide, etc. The critical step in this synthesis is the generation of the required stereochemistry at 22 and 23 position of the steroidal side chain which can be achieved by choosing the proper chiral auxiliary (*i.e.*, DHQD–CLB, dihydroquinine-*p*-chlorobenzoate). More recently, Brosa and co-workers[15] obtained an improved ratio of the desired stereoisomers, 2.6:1 by using dihydroquinidine-9-*O*-(9'-phenanthryl)ether (DHQD–PHN) as a chiral ligand and N-methylmorpholine-N-oxide as co-oxidant.



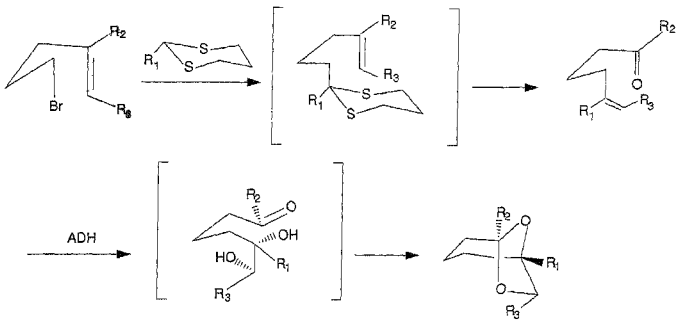
Brassinolide

McMorris and Patil[16] used an alternative route to synthesize 24-epibrassinolide from ergosterol using ADH reaction. The ratio of 22*(R)*, 23*(R)* diol increased greatly by using DHQD–CLB in *t*-BuOH/H_2O with $K_3Fe(CN)_6$–K_2CO_3 as co-oxidant and even better selectivity was observed using bisdihydroquinidiny-9-*O*-phthalazine, $DHQD_2$–PHAL(10:1) in favour of the desired diol. Santiago and Soderquist[17] and Turpin and Weigel[18] almost simultaneously used asymmetric dihydroxylation as the key step in a short and elegant synthesis of *(S)* (–)frontalin, the aggregation pheromone of southern pine beetle, although the approaches were slightly different as shown in Schemes 6 and 7.



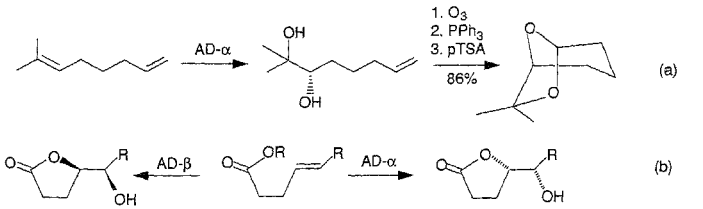
SCHEME 6.

A similar skeleton of 7,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane which is a constituent of a volatile aroma of beer was synthesized by Sharpless *et al*[19a] (Scheme 8a). Sharpless and



SCHEME 7.

co-workers[19b] also used ADH reaction towards a general approach for quick entry to several γ-lactones in high enantiomeric purity and applied this for a short synthesis of (–) and (+)-muricatacin, an acetogenin derivative that shows some cytotoxicity on human tumor cells (Scheme 8b).

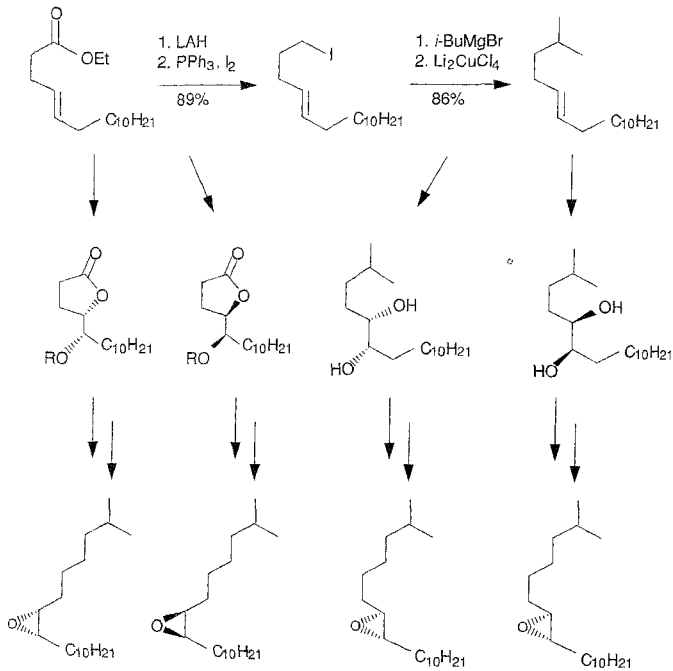


SCHEME 8.

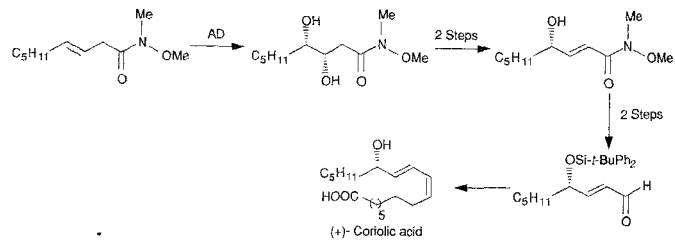
Keinan *et al*[20] have used ADH reaction for the synthesis of all the four isomers of disparlure, a sex attractant emitted by the female Gypsy moth, *Porthetria dispar*. The active pheromone is (+)-(7*R*,8*S*)-*cis*–7,8-epoxy-2-methyloctadecane which plays a significant role in the pest control. Here they report a convergent synthesis of all the possible isomers (Scheme 9).

Bennani and Sharpless[21] have achieved the synthesis of (+)-coriolic acid in which the resultant diol, obtained by ADH reaction of the desired β,γ-unsaturated amide, undergoes dehydration to furnish γ-hydroxy-α,β-unsaturated amide, which is finally transformed to (+)-coriolic acid (Scheme 10).

Crispino and Sharpless[22] reported the synthesis of juvenile hormone (III) in three steps

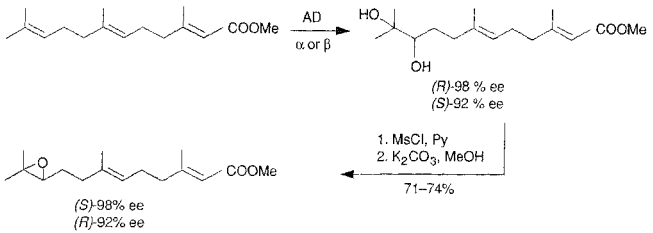


SCHEME 9.



SCHEME 10.

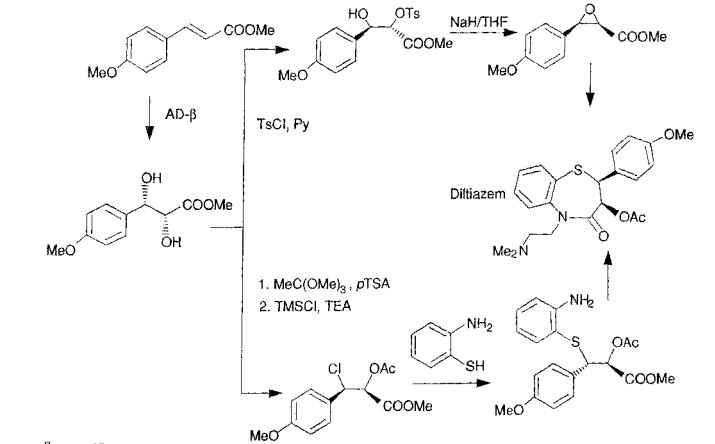
from methyl farnesoate using selective dihydroxylation followed by conversion of diol to epoxide (Scheme 11).



SCHEME 11.

2.2. *Drugs and drug intermediates*

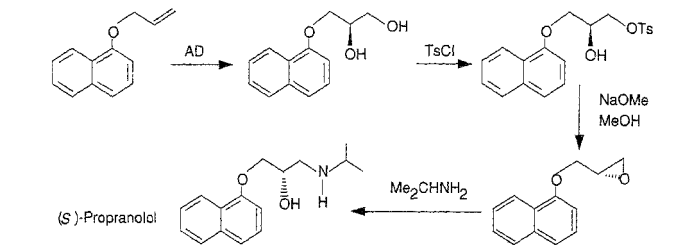
In Section 2.1, we have laid emphasis on the synthesis of several natural products and antibiotics which are biologically active and relevant molecules. In this section, we shall focus our attention on the synthesis of drug and drug intermediates. For example, Watson and co-workers[23] reported the first example of asymmetric dihydroxylation strategy towards the synthesis of a potent vasodialating agent, (+)-(2*S*,3*S*)-*cis*-diltiazem hydrochloride (Scheme 12). The diol was converted



SCHEME 12.

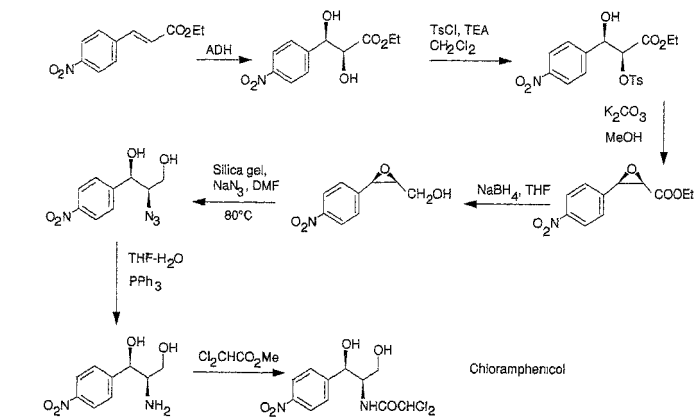
either into *cis*-epoxide or haloacetate which was then reacted with aminothiophenol to furnish *threo*-(2*S*,3*S*)thioether, a crucial intermediate in the synthesis of diltiazem.

Rama Rao *et al* [24] have prepared optically active(*S*)-propranolol using ADH reaction of α-naphthyl allyl ether, followed by conversion of diol to epoxide(Scheme 13). The epoxide was then converted into (*S*)-propranolol by a conventional method, *i.e.*, by treatment with isopropyl amine.



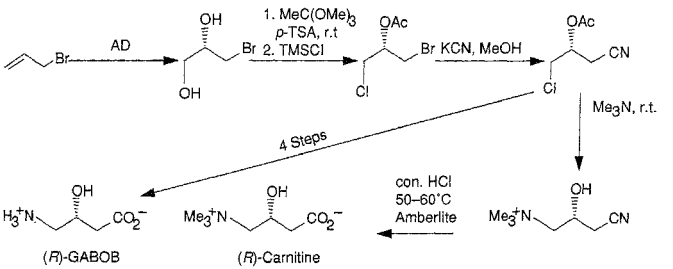
SCHEME 13.

Asymmetric synthesis of chloramphenicol has also been reported from the same research group[25] using both asymmetric epoxidation strategy as well as asymmetric dihydroxylation methodology with ethyl *p*-nitrocinnamate (Scheme 14).



SCHEME 14.

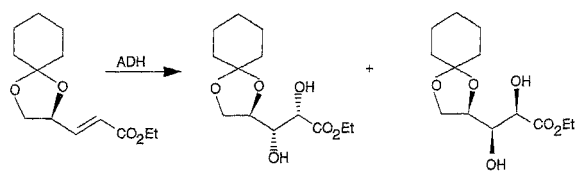
Sharpless and co-workers[26] have recently synthesized *(R)*-carnitine and *(R)*-γ-amino-β-hydroxybutyric acid (GABOB) which have potential usefulness as pharmaceuticals. GABOB is an antiepileptic and hypotensive drug and *(R)*-carnitine is a vitamin-like compound (Vitamin B_T), which is responsible for regulating the transport of long-chain fatty acids through mitochondrial membrane. Both these important class of compounds can be synthesized from a common intermedite (Scheme 15).



SCHEME 15.

2.3. Double diastereoselection and kinetic resolution

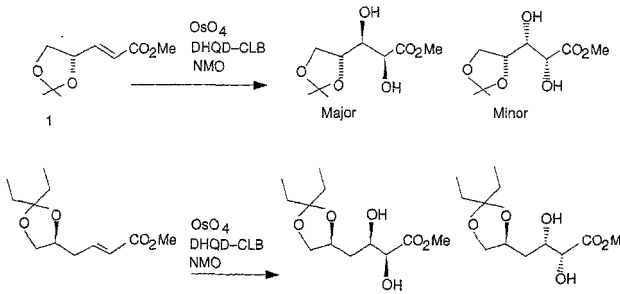
The concept of double diastereoselection[27] was introduced for ever-increasing demand of higher selectivity in stereoselective reactions. In asymmetric dihydroxylation of olefins also, the stereoselective outcome of the reactions get affected by the presence of a pre-existing chiral information in the substrate. This concept is usually exploited in kinetic resolution of a substrate using a chiral ligand. In matched cases where the chirality information of the reagent and substrate act synergitically, a higher order of stereoselectivity is usually observed. In contrast, if they exert their influence in opposite directions (mismatched cases) poor diastereoselectivity usually results. All the enzymatic or reagent-initiated kinetic resolutions are artifacts of this phenomenon and the extent of kinetic resolution depends on how best the match pair works synergitically and with what rate the reaction occurs. Annunziata *et al* [28] used this concept in asymmetric dihydroxylation of γ-chirality-substituted α,β-unsaturated



SCHEME 16.

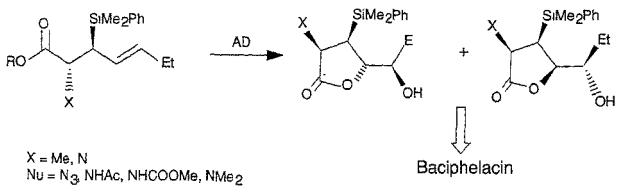
esters using DHQD–CLB as a chiral ligand in ADH reaction leading to >45:1 selectivity in favour of *anti*-diastereoselection (Scheme 16).

Sharpless and co-workers[29,30] have also reported an enhanced diastereoselectivity in the presence of an alkaloid derivative. For example, in the absence of DHQD–CLB, both substrates 1 and 2 showed poor diastereofacial bias, *i.e.*, 2.1:1 (for 1) and 1:1.1 (for 2), whereas in the presence of DHQD–CLB, they furnished 76 and 52% *de*, respectively (Scheme 17). More recently, the use of $(DHQD)_2$–PHAL enhanced the ratio of major isomers up to 39:1.



SCHEME 17.

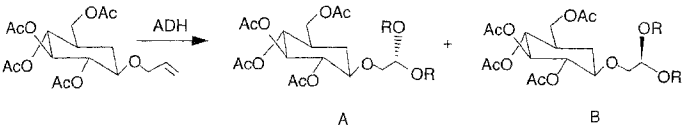
Ward and Procter[31] and Panek and Zhang[32] independently carried out double asymmetric induction using chiral allylsilanes. Initially, these authors carried out asymmetric dihydroxylation of *anti*-allylsilanes using various co-oxidants (Scheme 18).



SCHEME 18.

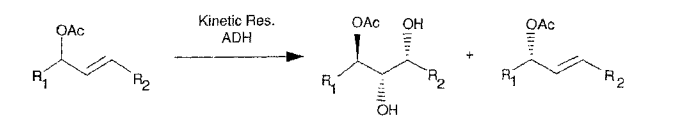
Using double stereodifferentiation method with DHQD–CLB for a matched pair and DHQ–CLB for a mismatched pair, the selectivity observed was 91:9 and 43:57, respectively. These lactones are used as key intermediates in the synthesis of baciphelacin, an antiviral, antileukemic antibiotic.

Gurjar and Mainkar[33] carried out asymmetric dihydroxylation of allyl D-glucopyranoside using DHQD–CLB and DHQ–CLB derivative to prepare chiral glycerol derivatives (Scheme 19).



SCHEME 19.

In the absence of a chiral auxiliary, the ratio of diastereomers (A:B) was found to be 65:35, which improved to 75:25 in the presence of DHQD–CLB, whereas the ratio decreased to 56:44 in the presence of DHQ–CLB, thus the former being a matched case and the latter a mismatched one. We have also carried out kinetic resolution of several racemic allylic acetates using $(DHQD)_2$–TP (bisdihydroquinidinyl terephthalate) and $(DHQ)_2$–TP as chiral auxiliaries by osmium-catalyzed asymmetric dihydroxylation reaction[34]. We observed that kinetic resolution of substrates is very much substituent dependent. Usually the ADH reaction of aromatic olefins show beneficial effect in determining the stereochemical bias; however, we observed that 1-acetoxy-1-cyclohexyl-3-phenyl-2-propene which has only one aromatic substituent attached to C=C bond showed the highest selectivity factor (S=25) leading to efficient kinetic resolution, whereas 1,3-diphenyl-3-acetoxylprop-1-ene exhibited the poorest kinetic resolution (Scheme 20). Interestingly, both the substrates are sterically nearly identical; however, the electronic nature of **1a** and **1b** plays a significant role in the large difference in



SCHEME 20.

kinetic resolution of **1a** and **1b**. These findings have been rationalized in terms of a model shown in Fig. 1 which suggests that π–π stacking interaction plays an important role in governing the facial selectivities of ADH reaction.

More recently, VanNienwenhze and Sharpless[35] have reported the kinetic resolution of *t*-butyl cyclohexene derivative (Scheme 21) using $(DHQD)_2$–PHAL or $(DHQ)_2$–PHAL as chiral

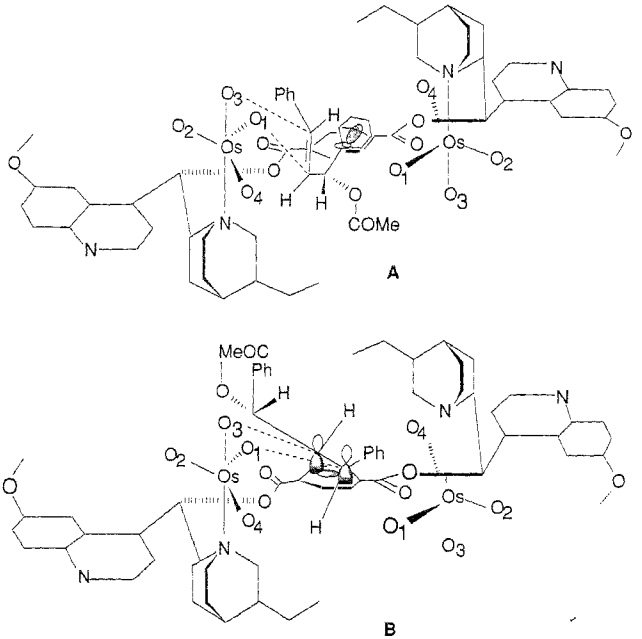
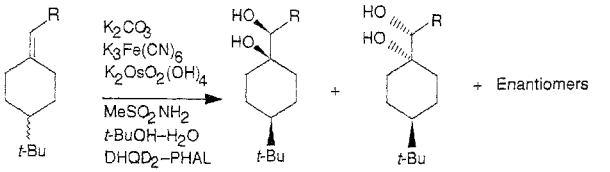


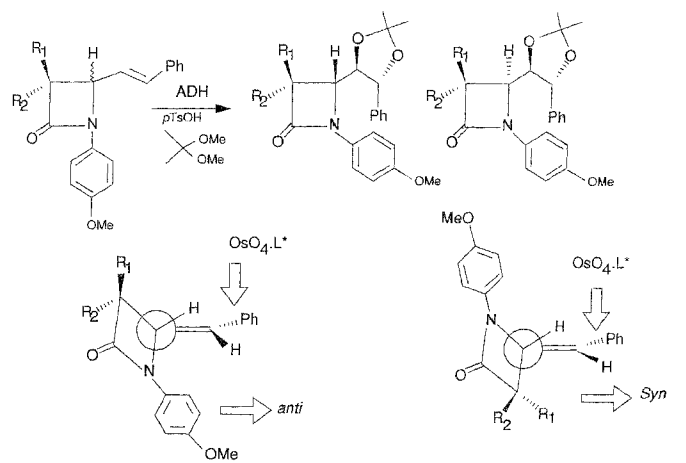
Fig 1 Transition state for the reaction of (A) *R*-allylic acetate, and (B) *S*-allylic acetate.



SCHEME 21

auxiliary. The maximum selectivity factor (*S*) was 32.0 using $(DHQD)_2$–PHAL as the catalyst.

Annunziata *et al*[36] have carried out asymmetric dihydroxylation of racemic 4-(2-styryl)-azetidin-2-one and found that *syn vs anti* attack on the azetidin-2-one ranges between 50:50 and 60:40; however, % ee of *syn* and *anti* products was achieved to a respectable level of selectivity (*ca* 80–94% ee). These authors attributed the poor diastereoselection in kinetic resolution of azetidin-2-one to the equal facility of attack by osmium reagent in the transition state (Scheme 22).



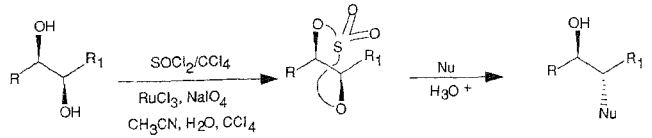
SCHEME 22.

2.7. Stereoselective transformation of diols

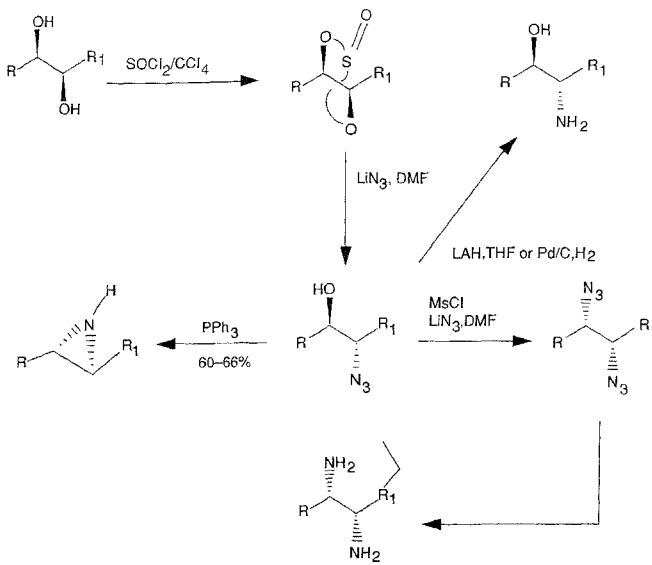
After the pioneering discovery of the catalytic asymmetric dihydroxylation of alkenes by Sharpless and co-workers, it was mandatory to demonstrate the utilities of these diols in synthetic organic chemistry. Gao and Sharpless[37], during the synthetic elaboration of these optically pure diols, discovered the usefulness of cyclic sulfate esters of 1,2-diols and reported stereoselective transformation of these diols to several other functional groups by a number of nucleophiles (Scheme 23).

The emerging utilities of cyclic sulfates and sulfites have been reviewed extensively[38] which gives a complete account up to July 1992 and hence this topic will not be covered in this review. Apart from cyclic sulfates, we have demonstrated[39] the usefulness of cyclic sulfites themselves as useful synthons for converting diols into several amino alcohols, and aziridines (Scheme 24).

During the last one year, a few more applications of cyclic sulfite and cyclic sulfate

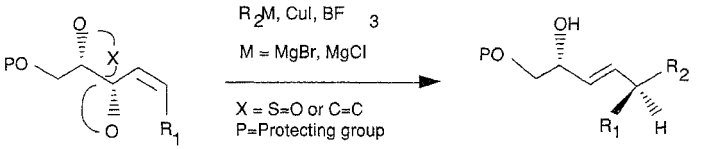


SCHEME 23.



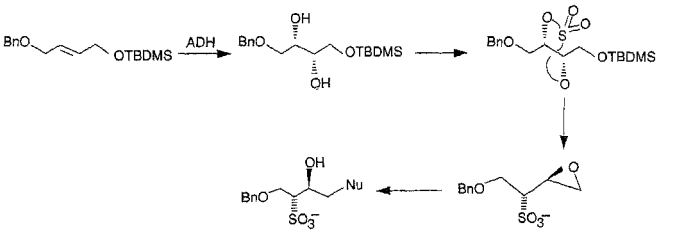
SCHEME 24.

chemistry have been reported which only will be highlighted. For example, Kang *et al* [40] have converted unsaturated vinylic diols to allylic cyclic carbonates, sulfites or sulfates and carried out nucleophilic attack at the allylic carbon using several organocuprate or Pd (O)-catalysed nucleophilic addition reaction affording high yields of optically active allylic alcohols (Scheme 25).



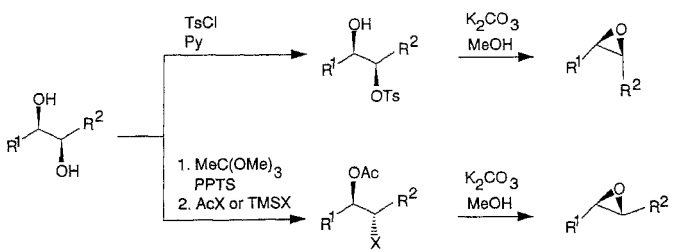
SCHEME 25.

More recently, Ko and Malik[41] have reported the synthesis of carbohydrates and related polyhydroxylated compounds employing asymmetric dihydroxylation followed by cyclic sulfate chemistry (Scheme 26).



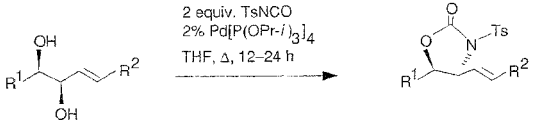
SCHEME 26.

Sharpless *et al*[42] have converted diols into *trans*-epoxides *via* monotosylate/bromohydrin (Scheme 27).



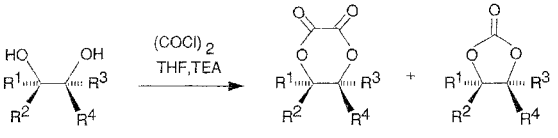
SCHEME 27.

Xu and Sharpless[43] have prepared oxazolidine-2-one by treating vinylic diols with tosylisocyanate in the presence of a catalytic amount of Pd(O) in refluxing THF (Scheme 28).



SCHEME 28

The most interesting feature of this transformation is the retention of configuration at both the stereogenic centers and this offers a good method for the preparation of *cis* amino alcohols. Iida and Itaya[44] treated several 1,2-diols with oxalyl chloride to furnish a mixture of cyclic carbonate and 1,4-dioxan-2,3-diones. The ratio of carbonate *vs* dioxane derivatives depends upon the nature of the substituent on the glycol moiety (Scheme 29).



SCHEME 29.

To summarize, the applications of asymmetric dihydroxylation of alkenes in synthetic organic chemistry is gaining ground slowly, even when the process to improve the selectivity in ADH reaction and understanding the origin of selectivity is continuing to evolve. We anticipate many more applications to emerge in the near future and this review just presents the state of art how a synthetic organic chemist can exploit this novel tool.

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References

1. MORRISON, J. D. *Asymmetric synthesis*, Vol. 5, 1985, Academic Press.
2. KATSUKI, T. AND SHARPLESS, K. B. *J. Am. Chem. Soc.*, 1980, **102**, 5974–5976.
3. JACOBSEN, E.N., MARKO, I., MUNGALL, W.S., SCHRODER, G. AND SHARPLESS, K. B. *J. Am Chem. Soc.*, 1988, **110**, 1968–1970.
4. LOHRAY, B. B. *Tetrahedron Asymmetry*, 1992, **3**, 1317–1349.
5. TOMIOKA, K., NAKAJIMA, M. AND KOGA, K. *J. Am Chem. Soc*, 1987, **109**, 6213–6215.

6	KELLY, T. R., BHUSHAN, V. AND LI, Q.	*Tetrahedron Lett*, 1990, **31**, 161–164.
7.	COOPER, A. J. AND SALOMON R. G.	*Tetrahedron Lett.*, 1990, **31**, 3813–3816.
8	ARJONA, O., CANDILEJO, A., DE DIOS, A., FERNANDEZ, R., PRADILLA, DE LA AND PLUMEL, J.	*J. Org Chem.*, 1992, **57**, 6097–6099.
9.	REITZ, A. B.	*ACS Symposium Series* 463, American Chemical Society, Washington, DC, 1991.
10.	HONDA, T., TOMITSUKA, K. AND TOUBUKI, M.	*J Org Chem.*, 1993, **58**, 4274–4279.
11.	IRELAND, R. E., WIPF, P. AND ROPER, T.D.	*J Org. Chem.*, 1990, **55**, 2284–2285.
12.	IKEMOTO, N AND SCHREIBER, S. L.	*J. Am Chem. Soc*, 1990, **112**, 9657–9659.
13.	KIM, B.M AND SHARPLESS, K.B.	*Tetrahedron Lett.*, 1990, **31**, 4317–4320.
14.	SUN, L.-Q. ZHOU,W –S. PAN, X.–F.	*Tetrahedron Asymmetry*, 1991, **2**, 973–976.
15.	BROSA, C., PERACAULA, R., PUIG, R. AND VENTURA, M.	*Tetrahedron Lett.*, 1992, **33**, 7057–7060.
16.	MCMORRIS, T. C AND PATIL, P.A.	*J. Org Chem.*, 1993, **58**, 2338–2339.
17.	SANTIAGO, B. AND SODERQUIST, J A.	*J Org Chem.*, 1992, **57**, 5844–5847.
18.	TURPIN, J. A. AND WEIGEL, L. O.	*Tetrahedron Lett*, 1992, **33**, 6563–6564.
19.a.	CRISPINO, G. A. AND SHARPLESS, K. B.	*Synlett*, 1993, 47–48.
b.	WANG, Z.-M., ZHANG, X.-L. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1992, **33**, 6407–6410.
20	KEINAN, K., SINHA, S.C., SINHA, A.–B., WANG, Z.-M., ZHANG, X.-L. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1992, **33**, 6411–6414.
21	BENNANI, Y. L. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1993, **34**, 2083–2086.
22.	CRISPINO, G. A. AND SHARPLESS, K. B.	*Synthesis*, 1993, 777–779.
23.	WATSON, K. G., FUNG, Y. M., GREDLEY, M., BIRD, G. J , JACKSON, W. R., UNTZOS, H. G. AND MATTHEWS, B. R.	*J. Chem Soc., Chem. Commun.*, 1990, 1018–1019.
24.	RAMA RAO, A.V., GURJAR, M. K. AND JOSHI, S. V.	*Tetrahedron Asymmetry*, 1990, **1**, 697–698.
25.	RAMARAO, A.V., PRAHLADARAO, S. AND BHANU, M. N.	*J. Chem Soc., Chem. Commun*, 1992, 859–860.
26.	KOLB, H. C., BENNANI, Y. L. AND SHARPLESS, K. B.	*Tetrahedron Asymmetry*, 1993, **4**, 133–141.
27.	MASAMUNE, S., CHOY, W., PETERSEN, J. S AND RITA, L. R.	*Angew. Chem. Int Ed. Engl.*, 1985, **24**, 1–30.
28.	ANNUNZIATA, R., CINQUINI, M., COZZI, F. AND RAIMONDI, L	*Tetrahedron*, 1988, **44**, 6897–6902.
29.	LOHRAY, B. B., KALANTER, T. H., KIM, B. M., PARK, C. Y., SHIBATA, T., WAI, J. S. M. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1989, **30**, 2041–2044.
30.	MORIKAWA, K. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1993, **34**, 5575–5578.
31.	WARD, R. A. AND PROCTER, G.	*Tetrahedron Lett.*, 1992, **33**, 3363–3366.

32.	PANEK, J. S. AND ZHANG, J.	*J Org Chem*, 1993, **58**, 294–296.
33.	GURJAR, M. K. AND MAINKAR, A. S.	*Tetrahedron Asymmetry*, 1992, **3**, 21–24.
34.	LOHRAY, B. B. AND BHUSHAN, V.	*Tetrahedron Lett.*, 1993, **34**, 3911–3914.
35.	VAN NIEUWENHZE, M. S. AND SHARPLESS, K. B.	*J Am Chem. Soc.*, 1993, **115**, 7864–7865.
36.	ANNUNZIATA, R., BENAGLIA, M., CINQUINI, M., COZZI, F. AND PONZINI, F.	*Bio-Org. Med. Chem. Lett*, 1993, (Personal Communication).
37.	GAO, Y. AND SHARPLESS, K. B.	*J Am. Chem. Soc.*, 1988, **110**, 7538–7539.
38.	LOHRAY, B. B.	*Synthesis*, 1992, 1035–1052.
39.	LOHRAY, B. B. AND AHUJA, J. R.	*J Chem. Soc, Chem Commun*, 1991, 95–97.
40.a	KONG, S.-K., PARK, Y.-W., LEE, D.-H., AND SIM, H.-S. AND JEON, J.-H.	*Tetrahedron Asymmetry*, 1992, **3**, 705–708.
b.	KANG, S.-K., LEE, D.-H., SIM, H.-S., AND LIM, J-S.	*Tetrahedron Asymmetry*, 1992, **3**, 1139–1140.
c.	KONG, S.-K., LEE, D.-H., SIM, H.-S., AND LIM, J.-S.	*Tetrahedron Lett.*, 1993, **34**, 91–94.
41.	KO, S.Y. AND MALIK, M.	*Tetrahedron Lett.*, 1993, **34**, 4675–4678.
42.a.	FLEMING, P. R AND SHARPLESS, K. B.	*J Org. Chem*, 1991, **56**, 2869–2875.
b.	OI, R. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1992, **33**, 2095–2098.
c.	KOLB, H. C. AND SHARPLESS, K. B.	*Tetrahedron*, 1992, **48**, 10515–10530.
43.	XU, D. AND SHARPLESS, K. B.	*Tetrahedron Lett.*, 1993, **34**, 951–952.
44.	IIDA, T. AND ITAYA, T.	*Tetrahedron*, 1993, **49**, 10511–10530.