surface carbonyls are several orders of magnitude more reactive in oxidative addition reactions with silanes than non-carbonyl-containing nickel samples.[17]

Destruction of solvent by the metal particles has been inferred from analysis of reaction products[18] in several of the methods used in producing active metal powders. Auger spectroscopy of nickel powders subjected to ultrasonic irradiation has indicated the presence of both surface carbon and significant quantities of surface oxygen (Ni:O rations of 1:2).[4]

The magnitude of the surface Raman signal tempts one to infer some surface enhancement of the Raman signal, and evidence for surface enhancement of the Raman spectrum for molecules adsorbed on nickel has precedent in the literature.[19,20] In the absence of an excitation profile, this conclusion is unwarranted, and the magnitude of the signal is attributed to the large surface area seen in the morphological experiments[13] and the large quantity of surface oxygen observed in the Auger experiment.[4]

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Inversion of Enantioselectivity in the Kinetic Resolution Mode of the Katsuki–Sharpless Asymmetric Epoxidation Reaction†

Seiichi Takano,* Yoshiharu Iwabuchi, and Kunio Ogasawara

Pharmaceutical Institute, Tohoku University
Aobayama, Sendai 980, Japan

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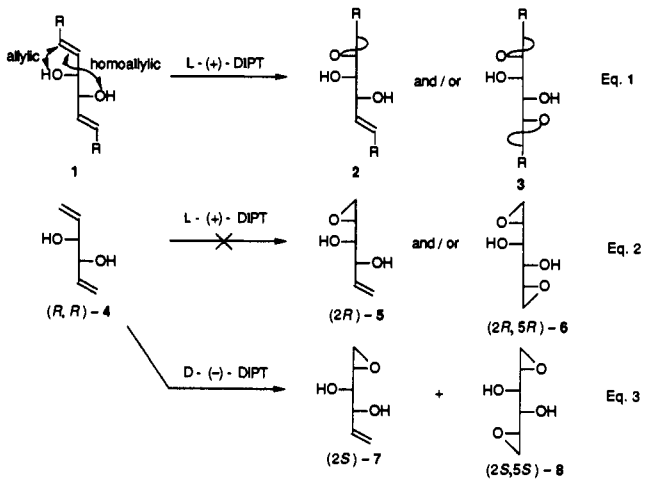
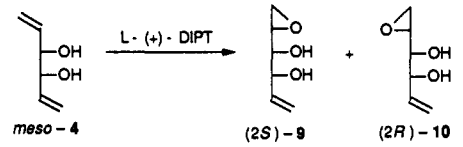
It is reported that the enantiofacial selection in the Katsuki–Sharpless asymmetric epoxidation[1,2] is opposite for allylic and homoallylic alcohols.[3,4] Since C_2-symmetric DL-1,2-dialkenylethylene glycols (**1**) may be regarded as either allylic or homoallylic substrates, we were intrigued by the possibility that an opposite stereogenic effect between the allylic and homoallylic relationships might synergistically amplify the enantiofacial selectivity in the chiral epoxidation of these symmetric substrates[5] (Scheme I, eq 1). We therefore examined the reaction of optically active C_2-symmetric (1*R*,2*R*)-1,2-divinylethylene glycol[6] [(*R*,*R*)-**4**], which led us to make a new and unexpected discovery relative to the Katsuki–Sharpless kinetic resolution process.

Since the empirical rule[1-4] embodied in asymmetric epoxidation predicts that 1*R*,2*R* glycol [(*R*,*R*)-**4**] would react at a much faster rate in the presence of diisopropyl L-(+)-tartrate [(+)-DIPT] to furnish *R* epoxide [(2*R*)-**5**] and/or *R*,*R* diepoxide [(2*R*,5*R*)-**6**],

Scheme I



Scheme II



we first carried out the reaction of (*R*,*R*)-**4** with *tert*-butyl hydroperoxide (TBHP) in the presence of a stoichiometric amount of (+)-DIPT and Ti(O-*i*-Pr)$_4$ and 4-Å molecular sieves[7] (Scheme I, eq 2). However, the reaction did not occur and the starting material was recovered unchanged. Surprisingly, when (−)-DIPT in place of (+)-DIPT was used (Scheme I, eq 3), the reaction took place facilely to afford *S* monoepoxide [(2*S*)-**7**] accompanied by a minor amount of *S*,*S* diepoxide [(2*S*,5*S*)-**8**] with 1.2 equiv of TBHP (Table I, entry 1) and the diepoxide [(2*S*,5*S*)-**8**] accompanied by a minor amount of the monoepoxide [(2*S*)-**7**] with 3 equiv of TBHP (Table I, entry 2). Correlation of the products with diethyl L-(+)-tartrate[8] and D-mannitol[9] established their stereochemistry unambiguously. This inversion of enantioselectivity and diastereofacial selectivity was also observed in the kinetic resolution of racemic DL substrate[10] [(±)-**4**] in the presence of (+)-DIPT, which furnished a mixture of *R* monoepoxide [(2*R*)-**7**], *R*,*R* diepoxide [(2*R*,5*R*)-**8**], and unreacted glycol [(*R*,*R*)-**4**] (Table I, entries 3 and 4).

Interestingly, the monobenzyl ether[11] of optically active DL substrate [(*R*,*R*)-**4**] was epoxidized only in the presence of (+)-DIPT to afford the monoepoxide with the *R* configuration, matching the prediction of the empirical rule (Table I, entry 5). When *meso*-1,2-divinylethylene glycol[10] [(*meso*)-**4**] was epoxidized for comparison in the presence of (+)-DIPT, the reaction occurred again in an unexpected mode to afford a 7:1 mixture of diastereomeric monoepoxides (2*S*)-**9** and (2*R*)-**10** (Scheme II) (Table I, entries 6–8), which could be separated after conversion into acetonides and correlated with (*S*)-*O*-benzylglycidol[12,13] to establish

† Dedicated to Professor George Büchi on the occasion of his 70th birthday.

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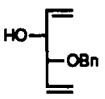
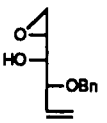
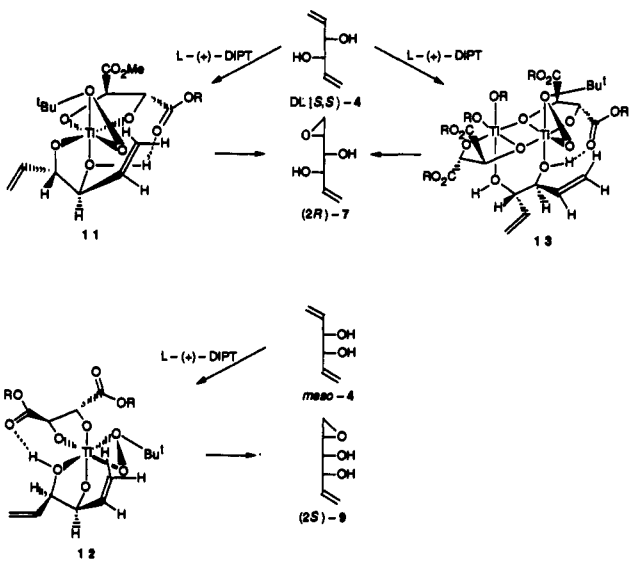
Table I. Katsuki–Sharpless Asymmetric Epoxidation of 1,2-Divinylethylene Glycols

entry	substrate	catalyst (equiv) Ti/tartrate[a]	TBHP	time, h	product, %[c] (corrected yield)	opt. yield, % ee
1	DL-(*R*,*R*)-**4**	1.0/1.2[a,d]	1.2	10	(2*S*)-**7**, 32 (42)	~100[e]
					(2*S*,5*S*)-**8**, 19 (25)	~100[e]
2	DL-(*R*,*R*)-**4**	1.0/1.2[a]	3.0	20	(2*S*)-**7**, 9 (10)	~100[e]
					(2*S*,5*S*)-**8**, 35 (40)	~100[e]
3	DL-(±)-**4**	1.0/2.0[b]	2.0	10	(*R*,*R*)-**4**, 47	~83[f]
					(2*R*)-**7**, 11	~100[h]
					(2*R*,5*R*)-**8**, 6	~100[h]
4	DL-(±)-**4**	1.0/2.0[b]	10	8	(*R*,*R*)-**4**, 36	~88[f]
					(2*R*)-**7**, 3	~100[h]
					(2*R*,5*R*)-**8**, 12	~100[h]
5		1.0/1.2[b,g]	5	12		~100[e]
6	*meso*-**4**	0.4/0.8[b]	10	114	**9**, 28 (60)	~90[h]
					10, 4 (9)	~90[h]
7	*meso*-**4**	1.0/2.0[b]	10	72	**9**, 45 (53)	~90[h]
					10, 6 (8)	~90[h]
8	*meso*-**4**	1.0/2.0[b]	30	90	**9**, 57 (71)	~90[h]
					10, 7 (10)	~90[h]
					60 (82)	

[a] D-(−)-DIPT. [b] L-(+)-DIPT. [c] Due to water solubility, the oxidation products could not be isolated completely from the reaction mixture. Corrected yields were estimated on the basis of consumed starting material. [d] Reaction did not take place with L-(+)-DIPT. [e] Estimated by ^{1}H NMR analysis (500 MHz). [f] Estimated by specific rotations. [g] Reaction did not take place with D-(−)-DIPT. [h] Estimated by ^{1}H NMR analysis (500 MHz) of MTPA esters.

Scheme III



their stereochemistry unambiguously.

To explain the unexpected stereochemical outcome encountered in the Katsuki–Sharpless asymmetric epoxidation of both DL and meso substrates, we assume involvement of the hexacoordinated complexes, **11** for DL-**4** and **12** for *meso*-**14**. In both of these, a near perpendicular alignment of the olefin axis and the epoxy chelate ring plane[14,15] may be preserved, leading to the corresponding epoxides in a stereospecific manner. Although the involvement of a dimeric complex,[2c,16] such as **13**, may also account for the stereochemical outcome observed in the DL substrate, a similar dimeric complex having the optimal stereoelectronic arrangement leading to (2*S*)-**7** seems unlikely from the meso counterpart (*meso*-**4**) (Scheme III).

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Supplementary Material Available: Schemes depicting various syntheses starting from (2*S*)-**7**, L-(+)-diethyl tartrate, (2*S*,5*S*)-**8**, D-mannitol, **9**, and **10** (2 pages). Ordering information is given on any current masthead page.

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(16) We thank one of referees for suggesting this complex.

Improving Two-Dimensional ^{1}H NMR NOESY Spectra of a Large Protein by Selective Deuteriation

Joseph Reisman,[†] Isabelle Jariel-Encontre,[‡] Victor L. Hsu,[†,§] Joseph Parello,[‡] E. Peter Geiduschek,[∥] and David R. Kearns*,[†]

Department of Chemistry and Department of Biology
University of California, San Diego
9500 Gilman Drive, La Jolla, California 92093-0342
Unité de Recherche Associée au CNRS, No. 1111
Faculté de Pharmacie, 15 avenue Charles Flahault
34060 Montpellier-Cédex, France

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The accurate determination of interproton distances, as obtained from 2D nuclear Overhauser effect experiments (NOESY), is of primary importance in the determination of solution-state protein structures by NMR, while 2D *J*-correlated experiments (COSY) are crucial for the assignment of specific spin-system resonances.[1-3]

[†] Department of Chemistry, University of California, San Diego.
[‡] Unité de Recherche Associée au CNRS.
[§] Present address: Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT 06510.
[∥] Department of Biology, University of California, San Diego.

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