The Mechanism and Stereochemistry of Asymmetric Transformation *via* Chiral Oxazolines

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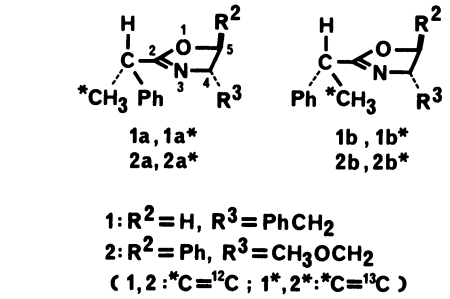
The stereoselectivity of asymmetric transformation of 2-substituted alkanoic acids *via* oxazolines was clarified by measuring the isomeric ratio of ^{13}C-labeled lithio oxazolines by ^{13}C NMR. The mechanism of the process was discussed from substituent effects of the oxazoline ring and solvent effects on the transformation.

Theoretically, asymmetric transformation of racemic compounds into a single optically active form is one of the best methods to obtain chiral substances.[1,2] However, suitable substances for the transformation have been practically limited to optically labile compounds such as atropisomers.[3]

In a previous paper,[4] we reported the asymmetric transformation of optically stable alkanoic acids into optically active form *via* chiral oxazolines. In the transformation, optically active alkanoic acids were obtained by metalation of oxazolines with butyllithium followed by quenching the lithio oxazolines by addition of water, and subsequent hydrolysis (Scheme 1). In this paper the mechanism and stereochemistry of the process will be discussed.

Oxazolines **1**, **2**, and ^{13}C-labeled **1**, **2** (**1***, **2***) were prepared according to the methods described previously,[4] and the epimers (**1a**, **1b**, **1a***, **1b***, **2a**, **2b**, **2a***, **2b***) were separated by silica-gel chromatography. Each epimer was submitted to the transformation separately. Deuterium oxide was used instead of water to quench the carbanions to assure the quantitative formation of carbanions (**I** and **II**). Thus, **1** and **2** were converted to the deuterated epimers (**1-d** and **2-d**) as shown in Scheme 2. The extent of asymmetric induction through the metallation and protonation process was monitored by GLPC analysis. The isomeric ratios of the intermediate lithio oxazolines were measured by ^{13}C NMR.



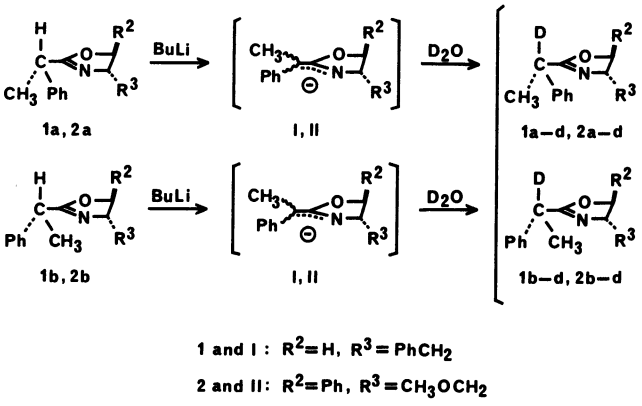
Scheme 1.

Experimental

IR spectra were measured with a JASCO A-3 spectrometer, mass spectra were recorded with a Hitachi M-80 mass spectrometer, optical rotations were measured with a JASCO Digital Automatic Polarimeter Model DIP-181. ^1H NMR spectra were obtained with a JNM-PS-100 spectrometer (100 MHz), and chemical shifts are expressed in δ downfield from TMS as an internal standard. ^{13}C NMR spectra were obtained with a JNM-FX-100 (25 MHz), and chemical shifts are reported in δ values relative to the β-THF signal which we defined as δ 25.0. GLPC analysis was carried out on a Shimadzu Gas Chromatograph GC-4CM equipped with a hydrogen flame ionization detector (column: OV-1 0.3 mm×50 m).

(4S)-2-(1-Phenylethyl)-4-benzyl-2-oxazoline (1a and 1b). A mixture of two epimers (**1a** and **1b**) was prepared from (4*S*)-(−)-2,4-dibenzyl-2-oxazoline and iodomethane according to the method described previously.[4] The two epimers were separated by silica-gel chromatography [silica gel 60 prepacked column (Merck), 40% ether–hexane].

1a: ^1H NMR ($CDCl_3$) δ=1.54 (3H, d, J=7 Hz, $C\underline{H}_3CH$),



Scheme 2.

2.66 (1H, dd, J=14 and 8 Hz, PhC$\underline{H}_2$), 3.11 (1H, dd, J=14 and 5 Hz, PhC$\underline{H}_2$), 3.71 (1H, q, J=7 Hz, $CH_3C\underline{H}$, 3.9—4.6 (3H, m), and 7.2—7.5 (10H, m).

1b: ^{1}H NMR ($CDCl_3$) δ=1.52 (3H, d, J=7 Hz, $C\underline{H}_3CH$), 2.66 (1H, dd, J=14 and 8 Hz, PhC$\underline{H}_2$), 3.13 (1H, dd, J=14 and 5 Hz, PhC$\underline{H}_2$), 3.72 (1H, q, J=7 Hz, $CH_3C\underline{H}$), 3.9—4.6 (3H, m) and 7.1—7.5 (10H, m).

Absolute Configuration of 1a and 1b. To determine the absolute configuration at C-2 *exo* methine of **1a** and **1b**, the mixture of **1a** and **1b** (**1a**:**1b**=10:90, 133 mg) was hydrolyzed in 3 M sulfuric acid (1 M=1 mol dm^{-3}). The configuration of the resulting 2-phenylpropionic acid [yield 88%; $[\alpha]_D^{25}$ −54.8° (*c* 1.6, $CHCl_3$) o.p. 72%] was the *R*-configuration.[5]

(4S)-2-(1-Phenyl[2-^{13}C]ethyl)-4-benzyl-2-oxazoline (1a and 1b*).* A mixture of ^{13}C-enriched **1a** and **1b** (**1a*** and **1b***) was prepared using *ca.* 50% enriched [^{13}C]-iodomethane by the method described previously.[4] The two epimers were separated by silica-gel chromatography as described above.

(4S,5S)-2-(1-Phenylethyl)-4-methoxymethyl-5-phenyl-2-oxazoline (2a and 2b). A mixture of two epimers (**2a** and **2b**) was prepared according to the method described by Meyers *et al.*[6] The two epimers were separated by silica-gel chromatography [C.I.G. prepacked column (Kusano Kagakukikai Co.), 1% ethanol-hexane].

2a: ^{1}H NMR ($CDCl_3$) δ=1.62 (3H, d, J=7 Hz, $C\underline{H}_3CH$), 3.40 (3H, s, $C\underline{H}_3O$), 3.6 (2H, m) 3.87 (1H, q, J=7 Hz, $CH_3C\underline{H}$), 4.1 (1H, m), 5.28 (1H, d, J=6 Hz, PhC$\underline{H}$O), and 7.1—7.5 (10H, m).

2b: ^{1}H NMR ($CDCl_3$) δ=1.60 (3H, d, J=7 Hz, $C\underline{H}_3CH$), 3.40 (3H, s, $C\underline{H}_3O$), 3.6 (2H, m), 3.87 (1H, q, J=7 Hz, $CH_3C\underline{H}$), 4.1 (1H, m), 5.25 (1H, d, J=6 Hz, PhC$\underline{H}$O), and 7.1—7.5 (10H, m).

Absolute Configuration of 2a and 2b. To determine the absolute configuration at C-2 *exo* methine of **2a** and **2b**, the mixture of **2a** and **2b** (6:94, 148 mg) was hydrolyzed in 6 M sulfuric acid. The configuration of the resulting 2-phenylpropionic acid [yield 85%; $[\alpha]_D^{34}$ −53.8° (*c* 1.6, $CHCl_3$) o.p. 70%] was the *R*-configuration.[5]

(4S,5S)-2-(1-Phenyl[2-^{13}C]ethyl)-4-methoxymethyl-5-phenyl-2-oxazoline (2a and 2b*).* A mixture of ^{13}C-enriched **2a** and **2b** (**2a*** and **2b***) was prepared using *ca.* 90% enriched [^{13}C]-iodomethane by the method described previously.[6] The two epimers were separated by silica-gel chromatography as described above.

Asymmetric Transformation of 1 in Tetrahydrofuran. The three mixtures of **1a** and **1b** [13.3 mg (0.05 mmol); **1a**:**1b**= 98:2, 49:51, 4:96] were prepared, and each mixture was dissolved in 1 ml of dry tetrahydrofuran under nitrogen atmosphere. Each solution thus prepared was cooled to −78 °C, and a solution of butyllithium (0.16 ml, 0.2 mmol) in hexane was added dropwise to the solution under stirring at −78 °C.[7] The reaction mixture was stirred for a given period (5, 45, and 300 min; the post metalation period) at −78 °C, and then 1 ml of 25% deuterium oxide-tetrahydrofuran solution was added and allowed to warm to room temperature. The mixture was extracted with ether, and the organic layer was washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The ratio of deuterated epimers (**1a-d** and **1b-d**) in this residue was determined by GLPC (170 °C), and deuterium incorporation was detected by Mass and ^{1}H NMR spectra. The results are shown in Table 1.

Asymmetric Transformation of 1 in 25% Hexamethlphosphoric Triamide-Tetrahydrofuran. The three mixtures of **1a** and **1b** [13.3 mg (0.05 mmol); **1a**:**1b**=98:2, 49:51, 4:96] were prepared, and each mixture was dissolved in 1 ml of dry 25% hexamethylphosphoric triamide-tetrahydrofuran under nitrogen atmosphere. The samples were treated as the method described for the asymmetric transformaiton of **1** in tetrahydrofuran, and in these reactions the post metalation period was 45 min. The results are shown in Table 2.

^{13}C NMR Measurements of Lithio Oxazolines of ^{13}C-Labeled 1. Five mixtures of ^{13}C-labeled epimers of **1** (**1a***:**1b***= 99:1, 74:26, 49:51, 26:74, 3:97) were prepared. Each mixture (26.6 mg, 0.1 mmol) was dissolved in 0.2 ml of dry tetrahydrofuran under nitrogen atmosphere, and 0.17 ml of butyllithium in hexane (1.2 M, 0.2 mmol) was added to the solution with stirring at −78 °C.[7] The ^{13}C NMR spectrum of each solution was recorded at −78 °C under quantitative conditions,[8,9] and showed a major peak at δ 16.1 (lithio oxazoline **IA***) and a minor peak at δ 18.1 (lithio oxazoline **IB***). After the measurment of the spectrum, 0.2 ml of 25% deuterium oxide-tertrahydrofuran solution was added to the sample at −78 °C. The ratio of the deuterated epimers (**1a*-d** and **1b*-d**) in the resulting mixture was determined by GLPC analysis as described before. The results are shown in Table 3.

^{13}C NMR Measurements of Lithio Oxazolines of ^{13}C-Labeled 2. Five mixtures of ^{13}C-labeled epimers of **2** (**2a***:**2b***= 95:5, 73:27, 54:46, 30:70, 2:98) were prepared. Each mixture (14.8 mg, 0.05 mol) was dissolved in 0.3 ml of dry tetrahydrofuran under nitrogen atmosphere, and 0.071 ml of butyllithium in hexane (1.4 M, 0.1 mmol) was added to the solution with stirring at −78 °C.[7] The ^{13}C NMR spectrum of each solution was recorded as described above, and showed two peaks at δ 15.8 (lithio oxazoline **IIA***) and δ 18.0 (lithio

TABLE 1. ASYMMETRIC TRANSFORMATION OF **1** IN THF

Post metalation period[a]/min	5		45		300	
1a:**1b**	**1a-d**:**1b-d**	*D*/%	**1a-d**:**1b-d**	*D*/%	**1a-d**:**1b-d**	*D*/%
98: 2	82:18	96	83:17	97	83:17	95
49:51	71:29	93	71:29	93	68:32	94
4:96	63:37	91	62:38	95	62:38	95

a) Samples were metalated at −78°C and stirred for the intervals indicated at −78°C.

TABLE 2. ASYMMETRIC TRANSFORMATION OF **1** IN 25% HMPA-THF

1a:**1b**	**1a-d**:**1b-d**	*D*/%[a]
98: 2	39:61	94
49:51	41:59	91
4:96	41:59	94

a) Post metalation period was 45 min.

TABLE 3. ASYMMETRIC TRANSFOMATION OF **1*** IN THF

1a*:**1b***	**IA***(δ16.1):**IB***(δ18.1)	**1a***-**d**:**1b***-**d**
99: 1	94: 6	85:15
74:26	83:17	80:20
49:51	73:27	73:27
26:74	66:34	69:31
3:97	55:45	62:38

oxazoline **IIB***). After the measurment of the spectrum, 0.1 ml of 25% deuterium oxide–tetrahydrofuran was added to the sample at −78°C. The ratio of the deuterated epimers (**2a*-d** and **2b*-d**) in the resulting mixture was determined by GLPC analysis as described before. The results are shown in Table 4.

(4R,5R)-2-(1-Phenylethyl)-4-methyl-5-phenyl-2-oxazoline (4). (4*R*,5*R*)-2-Benzyl-4-methyl-5-phenyl-2-oxazoline was prepared from (−)-norpseudoephedrine and ethyl 2-phenylacetimidate by the method described previously.[4] The obtained oxazoline was alkylated by iodomethane according to the method described by Meyers *et al.* to give **4**:[6] IR (neat 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (3H, d), 1.60 (3h, d), 3.8 (2H, m), 4.77 (1H, d), and 6.8—7.5 (10H, m); MS (70 eV) *m/z* (rel intensity) 265 (M^+; 2), 160 (19), 159 (86), 144 (23), 106 (5), 105 (100), and 77 (16).

(4R,5S)-2-(1-Phenylethyl)-4-methyl-5-phenyl-2-oxazoline (5). (4*R*,5*S*)-2-Benzyl-4-methyl-5-phenyl-2-oxazoline was prepared from (+)-norephedrine, and this oxazoline was alkylated to give **5** by the same method as described above: IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.74 (3H, d), 1.59 (3H, d), 3.8 (1H, m), 4.3 (1H, m), 5.37 (1H, d), and 6.8—7.4 (10H, m); *m/z* (rel intensity) 265 (M^+; 4), 160 (28), 159 (79), 144 (34), 105 (100), 79 (28), and 77 (33).

Hydrolysis of 4 and 5 before and after the Asymmetric Transformation. **4** and **5** were hydrolyzed before and after the asymmetric transformation as described previously to give chiral 2-phenylpropionic acid,[4] and the results are shown in Table 5.

Results and Discussion

Asymmetric Transformation of 1. After the asymmetric transformation of **1** in tetrahydrofuran, **1a** (98%) gave a deuterated mixture of **1a-d** and **1b-d** in a ratio of 8:2, and **1b** (96%) gave it in a ratio of 6:4 as shown in Table 1. In this transformation the configuration at C-2 *exo* methine of **1a** was retained *ca.* 80%, whereas in the case of **1b** inversion of the configuration predominated over retention of the configuration. This difference is not due to insufficient deprotonation from **1a** or **1b** because deuterium incorporation was above 90% in both cases. The post metalation period (stirring period of the reaction mixture after the addition of butyllithium) was varied in the range of 5 min, 45 min, and 300 min to examine the effect on the transformation. As shown in Table 1, ratios of the resulting epimers were practically independent on the post metalation period.

To clarify solvent effects, the transformation was performed in 25% hexamethylphosphoric triamide–tetrahydrofuran solution. The results are shown in Table 2. In this case, both **1a** (98%) and **1b** (96%) gave **1a-d** and **1b-d** in a ratio of 4:6 with deuterium incorporation above 90% in contrast with the results obtained in tetrahydrofuran.

These results indicate that the ratio of intermediate lithio oxazolines fomed in 25% hexamethylphosphoric triamide–tetrahydrofuran solution did not depend on that of **1a** and **1b**. On the other hand the ratio of the lithio oxazolines formed in tetrahydrofuran solution depended on that of starting epimers, and once they were formed the ratio did not change under the experimental conditions.

^{13}C NMR Measurment of Intermediate Lithio Oxazolines. This asymmetric transformation consists of the formation of lithio carbanions and successive protonation to them. To elucidate the mechanism of the process in tetrahydrofuran, the ratio of the lithio oxazolines was measured by ^{13}C NMR. In order to facilitate the ^{13}C NMR measurement, ^{13}C-enriched oxazolines (**1a*** and **1b***) were synthesized. The mixtures of **1a*** and **1b*** were prepared in various epimeric ratios and dissolved in tetrahydrofuran. Yellow solutions of lithio oxazolines were obtained by adding butyllithium. Two signals due to ^{13}C-enriched methyl carbon were observed at δ 16.1 (**IA***) and δ 18.1 (**IB***). After integration of these two signals (Table 3), the lithio oxazolines were quenched by deuterium oxide. ^1H NMR spectra showed that deuterium was incorporated to the *exo* methine carbon, α to the oxazoline ring. The ratios of the resulting deuterated **1a*-d** and **1b*-d** are summarized in Table 3.

The relationships between the ratio of **1a***:**1b*** and that of lithio oxazolines (**IA***:**IB***), and the ratio of lithio oxazolines and that of **1a*-d**:**1b*-d** are shown in Figs. 1 and 2, respectively.

Previously, the stereochemistry of the lithio carban-

Table 4. Asymmetric transformation of **2*** in THF

2a*:2b*	**IIA*(δ15.8):IIB*(δ18.0)**	**2a*-d:2b*-d**
95: 5	91: 9	76:24
73:27	76:24	70:30
54:46	67:33	66:34
30:70	54:46	60:40
2:98	37:63	53:47

Table 5. Hydrolysis of **4** and **5** before and after the asymmetric transformation

	Before the transformation				After the transformation			
	Yield %	$[\alpha]_D$[a]	O.p.[b] %	Config.	Yield %	$[\alpha]_D$[a]	O.p.[b] %	Config.
4	80	+0.7°	1	*S*	60	−13°	17	*R*
5	75	+1.5°	2	*S*	65	−26°	34	*R*

a) The concentrations at which the rotations were taken were *ca.* 2 g/100 ml in chloroform. b) Optical purities were based upon the highest literature values available: Ref. 5b; $[\alpha]_D^{25}$ +76.3° (*c* 1.6, $CHCl_3$).

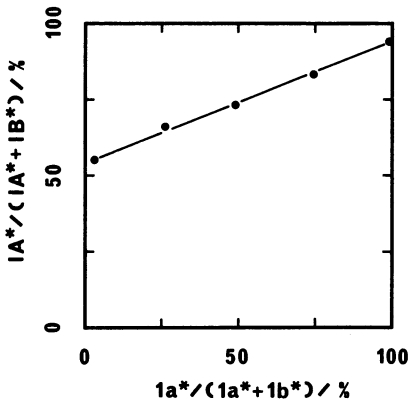


Fig. 1. Relationship between the ratio of **1a***:**1b*** and the lithio oxazoline ratio.

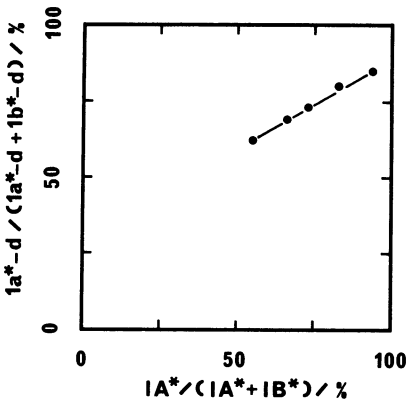


Fig. 2. Relationship between the lithio oxazoline ratio and the ratio of **1a***-d:**1b***-d.

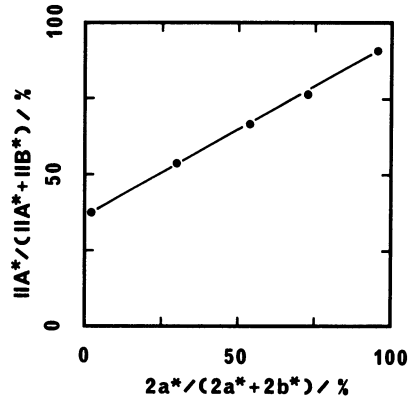


Fig. 3. Relationship between the ratio of **2a***:**2b*** and the lithio oxazoline ratio.

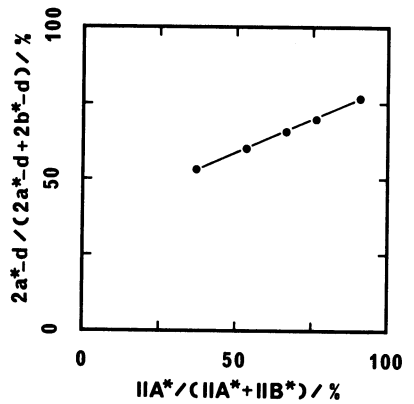


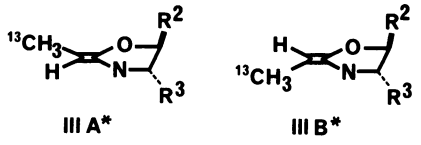
Fig. 4. Relationship between the lithio oxazoline ratio and the ratio of **2a***-d:**2b***-d.

ions of (4*S*,5*S*)-2-[2-^{13}C]ethyl-4-methoxymethyl-5-phenyl-2-oxazoline (**3***) were established by Meyers *et al.*[9] and Newcomb *et al.*[10] Therefore, (4*S*,5*S*)-2-(1-phenyl[2-^{13}C]ethyl)-4-methoxymethyl-5-phenyl-2-oxazoline (**2***), which has an analogous structure to **3*** and also to **1***, was prepared and treated in the same manner as described for **1*** to clarify the stereochemistry of the intermediate lithio oxazolines. Two signals due to ^{13}C-enriched methyl carbon of the lithio oxazoline were observed at δ 15.8 (**IIA***) and δ 18.0 (**IIB***). The results for the stereoselective transformation are summarized in Table 4, Fig. 3, and Fig. 4.

Stereochemistry of Intermediate Lithio Oxazolines. In the case of **1*** and **2***, ^{1}H NMR spectra showed that deuterium was incorporated to the *exo* methine carbon, α to the oxazoline ring. Two signals due to ^{13}C-enriched methyl carbon were observed for **1*** and **2***, respectively, in ^{13}C NMR spectra. These spectral data indicate that intermediate lithio oxazolines (**I, II**) exist as mixtures of *E*- and *Z*-isomers.

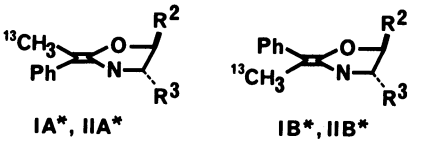
The relationship between the structure of lithio oxazoline of **3*** and the chemical shift of its ^{13}C-enriched methyl carbon was established by Meyers *et al.*[9] and Newcomb *et al.*[10] They assinged, in tetrahydrofuran solutions, a high field peak to **IIIA*** and a low field one to **IIIB***, respectively (Fig. 5).

According to the above structual assignment, in the



R^2=Ph, R^3=CH_3OCH_2

Fig. 5.



I*: R^2=H, R^3=$PhCH_2$

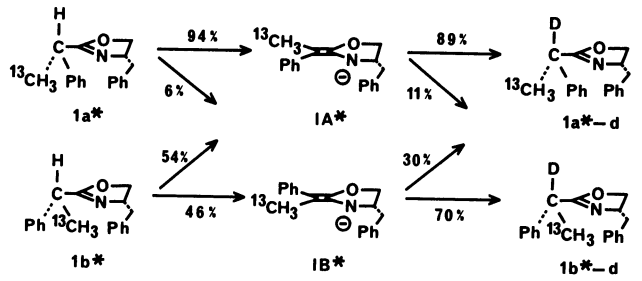
II*: R^2=Ph, R^3=CH_3OCH_2

Fig. 6.

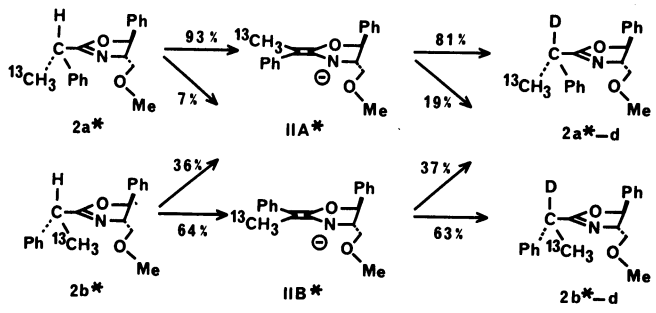
TABLE 6. CHEMICAL SHIFTS ASSIGNMENTS OF I*—III*

	ppm		ppm
IA*	16.1	**IB***	18.1
IIA*	15.8	**IIB***	18.0
IIIA*	10.9[a]	**IIIB***	11.7[a]

a) Ref. 9.



Scheme 3.



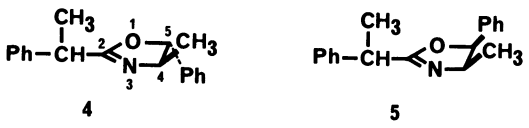
Scheme 4.

case of **1*** and **2***, lithio oxazolines **IA***, **IB***, **IIA***, and **IIB*** are assigned to the structures illustrated in Fig. 6 from their chemical shifts. Chemical sifts of ^{13}C-enriched methyl signals of **I*—III*** are summarized in Table 6.

Stereoselectivity of Asymmetric Transformation. The selectivities of the formation of the lithio oxazolines from **1*** and **2***, and that of deuterated epimers from the lithio oxazolines were calculated from the slopes of the straight lines in Figs. 1—4. Since the structures of lithio oxazolines were assigned as described above, the selectivities of the asymmetric transformation are illustrated in Schemes 3 and 4.

In the case of **1***, retention of the stereochemistry of **1a*** was explained by the selective formation of **IA*** from **1a*** and that of **1a*-d** from **IA***. Inversion of the stereochemstry of **1b*** was accounted for by the preferential formation of **IA*** from **1b*** and by the partial formation of **1a*-d** from **IB***. **2*** also showed the same trend of stereoselectivity to **1***. However in the case of **2***, the stereoselectivity of deuterium incorporation was slightly lower than that of **1***. This fact can be explained by the steric effect of substituents at oxazoline ring of **2*** which has a phenyl group on the oppsite side of a methoxymethyl group. The deuterium approach from the top side of the ring may be interfered to some extent by the phenyl group.

In both cases of **1*** and **2***, deuterium was incorporated from the top side of the oxazoline ring, and this stereoselectivity is seemed to be determined by steric effects at 4 position of the oxazoline ring. To elucidate the steric effects of substituents at 4 and 5 positions, asymmetric transformation of oxazolines **4** and **5** was examined. Configurations of the acids ob-



tained by hydrolysis of **4** and **5** after the asymmetric transformation were both *R*-configuration as shown in Table 5. Because the configuration of the resulting acids was not affected by the C-5 configuration, steric effects of a 5 positioned substituent was accounted to be smaller than that of a 4 positioned substituent.

From above results, at first deuterium is considered to approach stereoselectively to the nitrogen of the oxazoline ring, and in this approach the selectivity would be substantially affected by the 4 positioned substituents.

This stereoselective deuterium approach and the subsequent stereoselective deuterium transfer to the α carbon would result in the deuterium incorporation to the oxazoline anions (**I** and **II**) from the top side of the ring. This stereoselective process is well correspond to that observed in the asymmetric transformation of carbonyl compounds *via* enamines.[11]

References

1) H. B. Kagan and J. C. Fiaud, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, John Wiley & Sons, New York (1978), Vol. 10, p. 229.

2) H. Matsushita, M. Noguchi, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **48**, 3715 (1975).

3) M. M. Harris, "Progres in Stereochemistry," ed by W. Klyne and P. B. D. Mare, Butterworths Scientific Publications, London (1958), Vol. 2, p. 157.

4) S. Shibata, H. Matsushita, H. Kaneko, M. Noguchi, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **55**, 3546 (1982).

5) a) K. S. Y. Lau, R. W. Fries, J. K. Stille, *J. Am. Chem. Soc.*, **96**, 4983 (1974); b) S. P. Bakshi and E. E. Turner, *J. Chem. Soc.*, **1961**, 171.

6) A. I. Meyers, G. Knaus, K. Kamata, and M. E. Ford, *J. Am. Chem. Soc.*, **98**, 567 (1976).

7) Large excess amounts of butyllithium were used to exclude insufficient deprotonation from the oxazolines.

8) To assure quantitative conditions, the spin-lattice relaxation time (T_1) determination was performed for the β methyl carbon in **2a** and **2b** at −78°C using the standard inversion recovery techniques. The relaxation times of the β methyl carbon for both **2a** and **2b** were almost identical and equal to 0.25s. The ^{13}C NMR measurement was carried out using gated decoupling to suppress the Overhauser effect (NOE) [a delay time (τ)>5T_1].

9) A. I. Meyers, E. S. Snyder, and J. J. H. Ackerman, *J. Am. Chem. Soc.*, **100**, 8186 (1978).

10) M. A. Hoobler, D. E. Bergbreiter, and M. Newcomb, *J. Am. Chem. Soc.*, **100**, 8182 (1978).

11) H. Matsushita, Y. Tsujino, M. Noguchi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **51**, 201 (1978).