In another experiment 0.808 g of radioactive amine (59.35 mCi/mol) was deaminated. To the product, as diols, was added 50.0 mg of nonradioactive **8**. The compounds were separated by chromatography on alumina and 633 mg of products were recovered. The last fraction containing **8** was rechromatographed after adding nonradioactive **9** and 7-phenylnorbornane-2-*exo*,7-*syn*-diol as hold-back carrier. Diol **8** was then crystallized and assayed for carbon-14 content (18.78 mCi/mol). This corresponds to a yield of 1.85%.

Deamination of 7-*exo*-5-*d*.—Amine **7** containing deuterium in the 5-exo position (9.5 g) was deaminated as described before. After the products had been separated and crystallized, their nmr spectra were then taken to determine the position of the deuterium label. The signal for the 5-exo hydrogen (4.38 ppm, pyridine solution) of 2-*endo*-phenylnorbornane-2-*exo*,5-*endo*-diol (**11**) was absent. Also the signal for the 6-endo hydrogen (1.10 ppm) was collapsed to a pair of doublets.

In the spectrum of 2-*endo*-phenylnorbornane-2-*exo*,5-*exo*-diol (**10**)[21] the signal for the 5-endo hydrogen (3.98 ppm) was missing. Diol **9**, 2-*exo*-phenylnorbornane-2-*endo*,5-*exo*-diol, gave an nmr spectrum[2,21] in which the signal for the 4-bridgehead hydrogen (2.45 ppm) was missing and the signal for the 3-exo hydrogen (2.40 ppm) was collpased to a doublet.

The nmr spectrum of 2-*exo*-phenylnorbornane-2,5-*endo*-diol (**8**) was difficult to analyze. Therefore a sample of **8** weighing 100 mg was mixed with 50 mg of tris(dipivaloylmethane)europium and dissolved in deuteriochloroform. Under these conditions the spectrum was interpreted as follows (in parts per million): secondary hydroxyl hydrogen, 9.52 (br, 1 H); 2 and 6 aromatic hydrogens, 7.95 (m, 2 H); 3, 4, and 5 aromatic hydrogens, 7.45 (m, 3 H); 5-exo and tertiary hydroxyl hydrogens, unresolved, 6.98 (2 H); 3-endo hydrogen, doublet of doublets, 4.47 ($J_{3\text{-endo},3\text{-exo}}$ = 14.1, $J_{3\text{-endo},7\text{-anti}}$ = 2.8 Hz); the 3-endo hydrogen is partially overlapped by the 6-endo hydrogen, poorly resolved pair of triplets, 4.25 (2 H); 1- and 4-bridgehead hydrogens, unresolved 3.46 (2 H); 3-exo hydrogen, doublet of doublets, 3.03 ($J_{3\text{-exo},3\text{-endo}}$ = 14.1, $J_{3\text{-exo},4}$ = 4.4 Hz); the 3-exo hydrogen is partially overlapped by components of the 6-exo hydrogen, unresolved, 2.86 (2 H); 7-syn and 7-anti hydrogens, unresolved, 2.29 (2 H). In the spectrum for diol **8** derived from amine 7-*exo*-5-*d*, the signal for the bridgehead hydrogens at 3.46 ppm had an integrated intensity of 1.0. The signal for the 3-exo hydrogen collapsed to a pair of singlets with spacing of 14.1 Hz and the signal for the 5-endo hydrogen was narrower.

Registry No.—**5**, 29264-72-0; **6**, 29264-73-1; **7**, 29264-74-2; **7** oxime, 36808-83-0; **8**, 14518-60-6; **8** tosylate, 36808-85-2; **9**, 36808-86-3; **9** (phenyl-^{14}C), 36808-87-4; **11**, 36808-88-5; 2-*exo*-phenyl-2-hydroxy-5-norbanone, 36808-89-6; 2-*endo*-phenyl-2-hydroxy-5-norbanone, 36808-90-9.

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Sterically Controlled Syntheses of Optically Active Organic Compounds. XVI. Temperature Dependence of Hydrogenolytic Asymmetric Transamination[1]

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Temperature effects on the hydrogenolytic asymmetric transamination between ethyl pyruvate and optically active amines were studied. Definite temperature effects were observed between −20 and 65°. At relatively low temperature and when the optically active amine had an *R* configuration, the resulting alanine had an *R* configuration. The optical purity of (*R*)-alanine decreased as the reaction temperature increased and the configuration of analine inverted to the *S* configuration at higher temperature. Temperature effects using several optically active amines were studied. Within the context of these results, the possible steric course of the temperature-dependent asymmetric reactions is discussed. The differences of enthalpy of activation ($\Delta\Delta H^{\ddagger}_{S-R}$) and entropy of activation ($\Delta\Delta S^{\ddagger}_{S-R}$) between the formation of *S* amino acid and *R* amino acid were calculated at varying temperature. The results suggest that the entropy factor is very important in the inversion of configuration of the reaction product in the asymmetric synthesis.

Several studies on the hydrogenolytic asymmetric transamination between α-keto acids (or their esters) and optically active amino compounds have been reported.[2-8]

Generally, temperature is one of the most important factors in determining the molecular conformations that are involved in asymmetric syntheses. Some studies of the effect of temperature on asymmetric syntheses have been recorded in the literature.[9-15] In a previous communication,[16] the temperature effect on the hydrogenolytic asymmetric transamination between ethyl pyruvate and optically active amines was reported. This investigation examines further the temperature dependence of hydrogenolytic asymmetric transamination. The optically active amines used were (*S*)-(−)- and (*R*)-(+)-α-methylbenzylamine, (*R*)-(+)-α-ethylbenzylamine, and (*S*)-(−)-α-(1-naphthyl)ethylamine. The reaction temperatures used were in the range of −20 to 65°. The hydrogenation reactions were carried out at 1 atm of hydrogen by using palladium hydroxide on charcoal suspended in absolute alcohol with agitation provided by a magnetic stirrer. One series of the hydrogenation reactions

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TABLE I

TEMPERATURE EFFECT IN HYDROGENOLYTIC ASYMMETRIC TRANSAMINATION

Reaction[a]	Amine[b]	Temp, °C	Yield, %	Configuration	Alanine, $[\alpha]^{25}D$, deg, 5 *N* HCl	Optical purity,[c] %	DNP-alanine, $[\alpha]^{25}D$, deg, 1 *N* NaOH	Optical purity,[d] %
A 1	(*R*)-(+)-Me	+65	72	*S*	+5.3	36	+41.0	28
2	(*R*)-(+)-Me	+50	70	*S*	+6.1	42	+56.9	40
3	(*R*)-(+)-Me	+35	61	*S*	+5.0	34	+51.1	36
4	(*R*)-(+)-Me	+20	65	*S*	+1.3	9	+14.3	10
5	(*R*)-(+)-Me	+10	52	*R*	−2.1	14	−19.6	14
6	(*R*)-(+)-Me	0	52	*R*	−4.3	29	−49.5	34
7	(*R*)-(+)-Me	−10	68	*R*	−5.7	39	−56.7	39
8	(*R*)-(+)-Me	−20	54	*R*	−6.3	43	−81.4	57
1	(*S*)-(−)-Me	+65	68	*R*	−4.2	29	−44.9	31
2	(*S*)-(−)-Me	+50	63	*R*	−6.0	41	−62.4	43
3	(*S*)-(−)-Me	+35	68	*R*	−5.3	37	−53.2	37
B 4	(*S*)-(−)-Me	+20	58	*R*	−0.7	5	−6.0	4
5	(*S*)-(−)-Me	+10	65	*S*	−0.3	2	+16.0	11
6	(*S*)-(−)-Me	0	58	*S*	+2.5	17	+47.6	33
7	(*S*)-(−)-Me	−10	50	*S*	+5.1	35	+66.4	46
8	(*S*)-(−)-Me	−20	50	*S*	+8.3	57	+86.0	60
1	(*R*)-(+)-Et	+65	68	*S*	+5.1	35	+58.8	41
2	(*R*)-(+)-Et	+50	81	*S*	+8.0	55	+79.6	55
3	(*R*)-(+)-Et	+35	61	*S*	+6.0	41	+62.6	44
C 4	(*R*)-(+)-Et	+20	58	*S*	+1.4	10	+22.2	15
5	(*R*)-(+)-Et	+10	56	*R*	+2.6	18	−24.3	17
6	(*R*)-(+)-Et	0	54	*R*	−2.6	18	−26.2	18
7	(*R*)-(+)-Et	−10	54	*R*	−3.0	20	−42.1	29
8	(*R*)-(+)-Et	−20	58	*R*	−4.8	33	−60.7	42
1	(*S*)-(−)-Naph	+65	74	*R*	−0.7	5	−17.5	12
2	(*S*)-(−)-Naph	+50	74	*R*	+0.4	3	−2.8	2
3	(*S*)-(−)-Naph	+35	52	*S*	+3.5	24	+36.6	25
D 4	(*S*)-(−)-Naph	+20	52	*S*	+7.2	49	+73.1	51
5	(*S*)-(−)-Naph	+10	56	*S*	+8.1	56	+81.5	57
6	(*S*)-(−)-Naph	0	58	*S*	+9.3	64	+95.1	66
7	(*S*)-(−)-Naph	−10	38	*S*	+7.1	48	+82.2	57
8	(*S*)-(−)-Naph	−20	54	*S*	+8.5	58	+99.2	69
1	(*R*)-(+)-Me	+65	81	*S*	+3.3	23	+34.7	24
2	(*R*)-(+)-Me	+50	63	*S*	+1.8	12	+15.0	10
E 3	(*R*)-(+)-Me	+35	58	*R*	−4.4	30	−53.4	37
4	(*R*)-(+)-Me	+20	65	*R*	−3.1	21	−74.4	52
5	(*R*)-(+)-Me	+10	58	*R*	−8.8	60	−100.3	70
6	(*R*)-(+)-Me	0	52	*R*	−8.9	61	−102.7	71
7	(*R*)-(+)-Me	−10	49	*R*	−10.0	68	−105.1	73

[a] Absolute ethanol was used as a solvent in reactions A, B, C, and D. Ethyl acetate was used in reaction E. [b] (*R*)-(+)-Me, (*R*)-(+)-α-methylbenzylamine; (*S*)-(−)-Me, (*S*)-(−)-α-methylbenzylamine; (*R*)-(+)-Et, (*R*)-(+)-α-ethylbenzylamine; (*S*)-(−)-Naph, (*S*)-(−)-α-(1-naphthyl)ethylamine. [c] Defined as $[\alpha]D$ obsd/$[\alpha]D$ lit. × 100; (*S*)-(+)-alanine, $[\alpha]^{25}D$ −14.6° (5 *N* HCl). [d] Defined as $[\alpha]D$ obsd/$[\alpha]D$ lit. × 100; DNP-(*S*)-(+)-alanine, $[\alpha]^{25}D$ +143.9° (1 *N* NaOH).

was carried out with ethyl acetate as the solvent. The results are summarized in Table I and in Figures 1 and 2.

The consumption curves of hydrogen at different temperatures are shown in Figure 1. The hydrogenation reaction in ethanol suspension takes place rapidly at temperatures higher than 0°. At temperatures below −20°, the hydrogenation reaction proceeds slowly. At −30°, the rate of the hydrogenation reaction was very slow. When ethyl acetate was substituted for the ethanol, the hydrogenation reaction at −20° was extremely slow.

In reactions A and B reported in Table I and Figure 2, alanine was prepared by using (*R*)-(+)-α-methylbenzylamine and (*S*)-(−)-α-methylbenzylamine at temperatures from −20 to 65°. Within this temperature range, the optical activity of alanine that was prepared from (*R*)-(+)-α-methylbenzylamine was opposite in sign and almost identical in magnitude with that of the alanine that was prepared from (*S*)-(−)-α-methylbenzylamine (Figure 2). At lower temperature, the configuration of alanine that was prepared from the (*R*)-(+) amine was found to be *R* (optical purity 57% at −20°). As the temperature of the reaction was increased, the optical activity decreased sharply. The optical activity of alanine became zero at about 17°. The configuration of alanine then inverted and the optical activity of (*S*)-alanine increased steadily until a maximum was reached at about 45–50° (optical purity 45% at 50°). Finally, the optical activity of alanine decreased at higher temperatures (Figure 2). The sigmoidal shapes of optical purity curves of alanine prepared from the other optically active amines are similar.

Formation of optically active compounds in the asymmetric synthesis is due to the difference between the rates of formation of the two diastereomers from the starting material (substrate*). The rates of formation of the diastereomeric activated complexes are determined by the difference of the free energies of

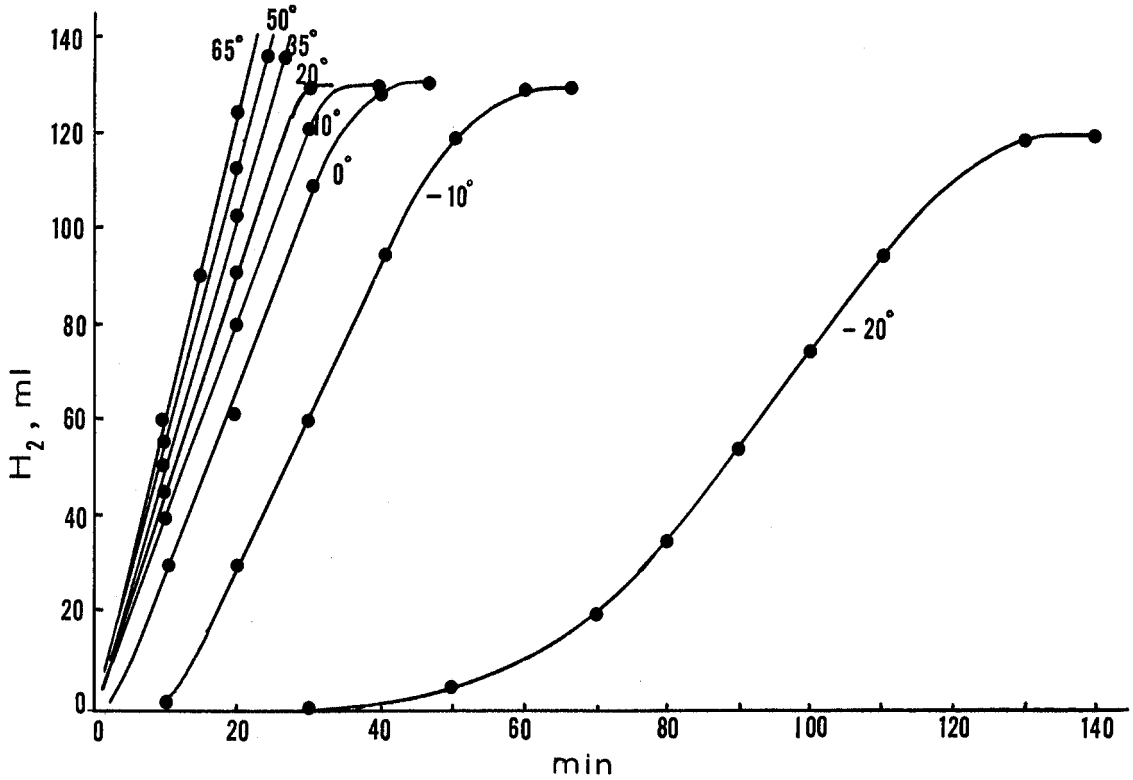
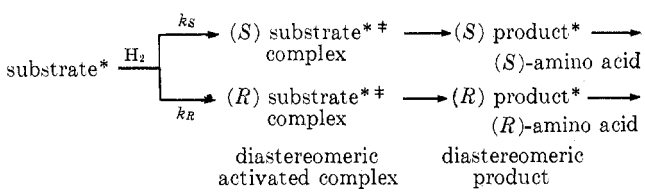


Figure 1.—Hydrogen consumption in the hydrogenation and hydrogenolysis of the Schiff base prepared from ethyl pyruvate and (*S*)-(−)-α-methylbenzylamine (reaction B).

activation ($\Delta G^{\pm}$) for the two diastereomeric transition states. According to the transition-state theory,[17]



the rate of formation of the [(*S*) substrate* complex]$^{\pm}$ is expressed as follows.[10,17-20]

$$k_S = \kappa_S \frac{kT}{h} e^{-\Delta G_S^{\pm}/RT}$$

If we assume that the transmission coefficient κ_S is equal to κ_R, the (*S*) product*/(*R*) product* is expressed as shown below.

$$\frac{(S)\text{ product*}}{(R)\text{ product*}} = (S)/(R) = k_S/k_R =$$

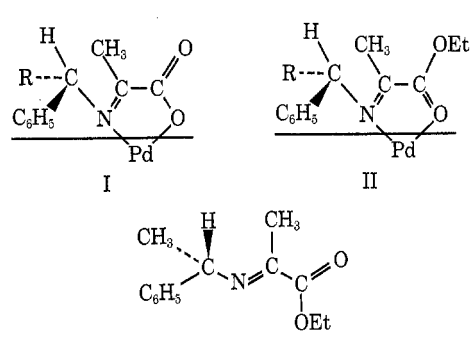
$$\exp\frac{\Delta S_S^{\pm} - \Delta S_R^{\pm}}{R} \exp\frac{-(\Delta H_S^{\pm} - \Delta H_R^{\pm})}{RT}$$

$$= \exp\frac{\Delta\Delta S^{\pm}_{S-R}}{R} \exp\frac{-\Delta\Delta H^{\pm}_{S-R}}{RT}$$

$$\log (S)/(R) = \log k_S/k_R = \frac{\Delta\Delta^{\pm}_{S-R}}{2.3R} - \frac{\Delta\Delta HS^{\pm}_{S-R}}{2.3RT}$$

Figure 3 shows the plot of log (*S*/*R*) against 1/*T* from the result obtained in the asymmetric transamination reactions. From this plot, $\Delta\Delta H^{\pm}_{S-R}$ and $\Delta\Delta S^{\pm}_{S-R}$ at varying temperatures were calculated. These are summarized in Table II. At low temperatures (−20 to 10°), $\Delta\Delta H^{\pm}_{S-R}$ is low; however, $\Delta\Delta S^{\pm}_{S-R}$ is higher. At relatively higher temperatures (10–50°), $\Delta\Delta H^{\pm}_{S-R}$ increases some, but $\Delta\Delta S^{\pm}_{S-R}$ increases considerably. At higher temperatures (50–65°), the signs of $\Delta\Delta H^{\pm}_{S-R}$ and $\Delta\Delta S^{\pm}_{S-R}$ change and their absolute values both decrease except for the case using (*S*)-(−)-α-(1-naphthyl)ethylamine. These results strongly suggest that the temperature-dependent asymmetric synthesis is largely controlled by the entropy factor ($\Delta\Delta S^{\pm}_{S-R}$). This indicates that the conformations of two diastereomers in the transition state are quite different and the entropy of activation of one diastereomer which leads to (*S*)-amine-(*S*)-amino acid is much lower than that of other diastereomers (*S*)-amine-(*R*)-amino acid which resulted in the formation of (*R*)-amino acid.

On the other hand, in the previous paper from this laboratory, a possible steric course of the hydrogenolytic asymmetric transamination was discussed.[5,8] As shown in structure I or II, the possible preferred conformation



I II

III

(17) S. Glasston, K. J. Laidler, and H. Eyring, "The Theory of Rate Process," McGraw-Hill, New York, N. Y., 1941.

(18) E. I. Klabunovskii and E. S. Levitina, *Russ. Chem. Rev.*, **39**, 1035 (1970).

(19) The $\Delta G^{\pm}$ of the equation includes external factors such as solvents and catalysts, which cause a change in the free energy of activation of the reactions; *cf.* Chapters 4 and 8 of ref 17.

(20) C. A. Eckert, *Ind. Eng. Chem.*, **59**, 20 (1967).

TABLE II

$\Delta\Delta H^{\ddagger}_{S-R}$ AND $\Delta\Delta S^{\ddagger}_{S-R}$ OF THE REACTIONS AT VARYING TEMPERATURES

		−20 to 0°		0–35°		50–65°	
Chiral center	Solvent	$\Delta\Delta H^{\ddagger}_{S-R}$, kcal mol^{-1}	$\Delta\Delta S^{\ddagger}_{S-R}$, cal mol^{-1} deg^{-1}	$\Delta\Delta H^{\ddagger}_{S-R}$, kcal mol^{-1}	$\Delta\Delta S^{\ddagger}_{S-R}$, cal mol^{-1} deg^{-1}	$\Delta\Delta H^{\ddagger}_{S-R}$, kcal mol^{-1}	$\Delta\Delta S^{\ddagger}_{S-R}$, cal mol^{-1} deg^{-1}
(*R*)-(+)-Me	EtOH	4.1	13.8	7.2	25.0	−3.1	−7.7
(*S*)-(−)-Me	EtOH	−5.4	−18.0	−7.2	−25.0	2.7	10.2
(*R*)-(+)-Et	EtOH	3.6	14.6	6.1	21.6	−4.0	−9.9
(*S*)-(−)-Naph	EtOH	−2.2	5.3	−6.6	−20.6	−6.6	−20.6
(*R*)-(+)-Me	ACOEt	1.1	0.4	8.9	28.0	3.1	9.4

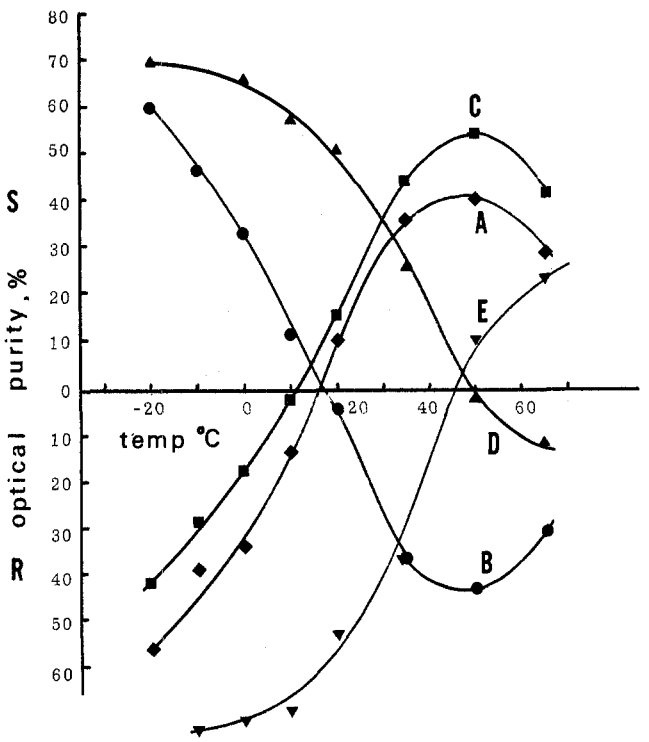


Figure 2.—Temperature effect in hydrogenolytic asymmetric transamination: A, (*R*)-(+)-α-methylbenzylamine, in ethanol; B, (*S*)-(−)-α-methylbenzylamine, in ethanol; C, (*R*)-(+)-α-ethylbenzylamine, in ethanol; D, (*S*)-(−)-α-(1-naphthyl)ethylamine, in ethanol; E, (*R*)-(+)-α-methylbenzylamine, in ethyl acetate.

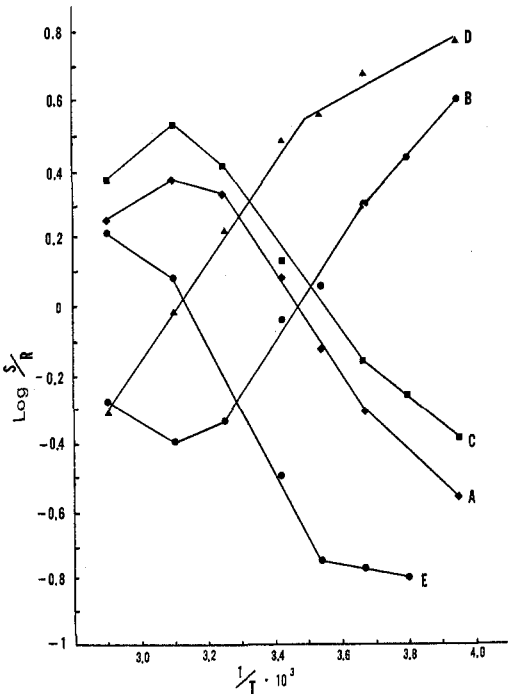


Figure 3.—Temperature dependence of hydrogenolytic asymmetric transamination.

of the substrate at room temperature could be a five-membered cyclic complex with the catalyst (chelation hypothesis) depending on whether the substrate is an acid (I) or its ester (II). These chelated substrates with the catalyst could then be adsorbed on the catalyst surface at the less bulky side of the molecule and the catalytic hydrogenation reaction would take place. The proposed steric course was supported by the results obtained in the study of various optically active amines and also in the study of the solvent effect on the asymmetric synthesis.[6,8]

In reaction C in Table I and Figure 2, the optical purity of alanine prepared from (*R*)-(+)-α-ethylbenzylamine is lower than that of alanine prepared from (*R*)-(+)-α-methylbenzylamine at a lower temperature. On the other hand, the optical purity of alanine prepared from (*S*)-(−)-α-(1-naphthyl)ethylamine is much higher at lower temperatures. These findings could be explained by the possible steric course proposed earlier (chelation hypothesis).[5,8] The preferred conformation of the substrate on the catalyst surface at lower temperatures would be structure II. The five-membered cyclic intermediate (II) with the catalyst would then be adsorbed at the less bulky side of the molecule and then hydrogenation would take place in a two-step mechanism. The participation of structure II would decrease as the reaction temperature increased. Concomitantly, the participation of the nonchelated structure III would increase. At higher temperature the preferred conformation would be structure III, which was hydrogenated without forming a five-membered substrate–catalyst complex (one-step mechanism). The decrease in optical purity at higher temperatures could be explained by the thermal agitation of the conformation of the substrate molecule.

If this is the case, the temperature dependence of the optical purity of alanine using α-methylbenzylamine, α-ethylbenzylamine, and α-(1-naphthyl)ethylamine can be understood without any contradiction in the results of the present and previous studies. At a relatively low temperature, the optical purity of alanine prepared from (*R*)-(+)-α-methylbenzylamine (reaction A) is higher than that of alanine prepared from (*R*)-(+)-α-ethylbenzylamine (reaction C), because the relative bulkiness of phenyl residue to methyl residue (reaction A) is larger than that of phenyl residue to ethyl residue (reaction C) in structure II. At a relatively high temperature (40–50°), the optical purity of alanine prepared from (*R*)-(+)-α-ethylbenzylamine (reaction C) is higher than that of alanine prepared from (*R*)-(+)-α-methylbenzylamine (reaction A). This could be

explained by the fact that the relative bulkiness of the ethyl group to the hydrogen is larger than that of the methyl group to the hydrogen in structure III. Similarly, at a relatively low temperature, the optical activity of alanine from (*S*)-(−)-α-(1-naphthyl)ethylamine (reaction D) is much higher than that of alanine from (*S*)-(−)-α-methylbenzylamine (reaction B). This could be explained by the fact that the naphthyl group is much bulkier than the phenyl group in structure II. Even at a relatively higher temperature, the stronger interaction of the naphthyl group with the catalyst might stabilize the conformation of structure II. Structure III would contribute to the inversion of configuration of the product at higher temperature. However, the relative bulkiness of the naphthyl group is so large that the sterically controlled effect based on the relative bulkiness of the hydrogen and methyl group in structure III might not function effectively. The thermal molecular movement of the substrate at higher temperature (>50°) would also result in lower optical purity.

All reactions described above were carried out by using absolute alcohol as the solvent. The reaction E in Figure 2 shows a temperature effect of alanine from (*R*)-(+)-α-methylbenzylamine in alcohol and in ethyl acetate. A definite solvent effect of varying temperatures is observed. At a relatively low temperature, the optical purity of alanine prepared in ethyl acetate is much larger than that of alanine prepared in ethanol. This could be explained by the solvent effect that is discussed in the previous paper.[6,8] At a relatively low temperature, the preferred conformation would be structure II in a solvent that has a low dielectric constant. Interactions between substrate and catalyst would be stronger in a less polar solvent than in a polar solvent. As indicated by the experimental results for reaction E, even at a relatively higher temperature (~45°), the preferred conformation of the substrate would be structure II.

This explanation of the steric course of the asymmetric reactions is consistent with the experimental values of $\Delta\Delta H^{\ddagger}_{S-R}$ and $\Delta\Delta S^{\ddagger}_{S-R}$ at varying temperatures.

In order to avoid possible fractionation of partially optically active alanine during the course of isolation and purification, the crude alanine that was isolated by the use of an ion exchange column was converted to a DNP derivative. The DNP-alanine was then purified by using Celite column chromatography[21] without fractionation of the optical isomers.[5,8]

(21) J. C. Perrone, *Nature (London)*, **167**, 513 (1951); A. Court, *Biochem. J.*, **58**, 70 (1954).

Experimental Section

All hydrogenation and hydrogenolysis were carried out in a three-neck flask at 1 atm with magnetic stirring. The palladium hydroxide on charcoal catalyst used in all experiments was from a single preparation. Hydrogenolysis was carried out with a Parr 3910 shaker-type hydrogenation apparatus. All optical activity measurements were carried out on a JASCO-ORD-CD-UV 5 spectropolarimeter. The accuracy of reaction temperatures is about ±1°.

All experimental procedures were similar to those described in an earlier paper[8] except for the hydrogenation apparatus and reaction temperature.

The specific rotations of optically active amines used follow: (*R*)-(+)-α-methylbenzylamine, $[\alpha]^{25}D$ +41.5° (benzene); (*S*)-(−)-α-methylbenzylamine, $[\alpha]^{25}D$ −42.3° (benzene); (*R*)-(+)-α-ethylbenzylamine, $[\alpha]^{25}D$ +21.7° (benzene); (*R*)-(+)-α-(1-naphthyl)ethylamine, $[\alpha]^{25}$ +88.0° (benzene).

Alanine from Ethyl Pyruvate and (*R*)-(+)-α-Methylbenzylamine (Reaction A, 1).—Ethyl pyruvate (0.58 g, 0.005 mol) and (*R*)-(+)-α-methylbenzylamine (0.61 g, 0.005 mol) were dissolved in 30 ml of benzene at room temperature. The precipitated water was removed by adding anhydrous sodium sulfate. The benzene solution was evaporated under reduced pressure after filtration. The remaining crude Schiff base was dissolved in 30 ml of absolute ethanol and the solution was subjected to hydrogenation at 1 atm by the use of 0.5 g of palladium hydroxide on charcoal at 65°. The hydrogenated and hydrogenolyzed product was hydrolyzed by refluxing with 30 ml of 6 *N* HCl for 5 hr and was dried under reduced pressure. The dried hydrolysate was dissolved in 10 ml of water and the solution was applied to a Dowex 50 × 2 column (hydrogen type, 50–100 mesh, 25 × 1.8 cm) and eluted with 1.5 *N* aqueous ammonia: yield 320 mg (72%); $[\alpha]^{25}D$ +5.25° (*c* 4.53, 5 *N* HCl); optical purity, 36%. After recrystallization from water and ethanol, an elemental analysis of alanine was carried out. *Anal.* Found: C, 40.70; H, 7.82; N, 15.44.

A part of the unrecrystallized alanine was converted to DNP-alanine in a conventional manner. The DNP-alanine obtained was purified by the use of a Celite column treated with pH 7 citrate–phosphate buffer (0.2 *M*).[21] These procedures are similar to those described in earlier reports.[5,8]

DNP-alanine had mp 168–169° dec, $[\alpha]^{25}D$ +41.0° (*c* 2.39, 1 *N* NaOH), optical purity 28.5%. The DNP-alanine was recrystallized from ether and petroleum ether (bp 30–60°) for elemental analysis, mp 172–174°. *Anal.* Found: C, 42.50; H, 3.58; N, 16.46.

Registry No.—(*R*)-(+)-α-Methylbenzylamine, 3886-69-9; (*S*)-(−)-α-methylbenzylamine, 2627-86-3; (*R*)-(+)-α-ethylbenzylamine, 3082-64-2; (*R*)-(+)-α-(1-naphthyl)ethylamine, 3886-70-2; (*S*)-alanine, 56-41-7; (*R*)-alanine, 338-69-2; (*S*)-DNP-alanine, 1655-52-3; (*R*)-DNP-alanine, 6367-22-2.

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