yield); mol wt 207; ir (CCl_4) 1734 (s), 928 (m); nmr 5.26 and 4.94 (2 H, 2 m, terminal vinylic H), 2.2 (2 H, m, α H), 1.19, 1.15, 0.92 (9 H, 3 s, methyl H). Except for the vinylic region (4.6–6.2), the nmr spectrum of **11** was identical with that of **2**.

The other photoproducts from **8** were not isolated but according to glc the irradiation of **8** closely paralleled the irradiations of **1** and **6**.

Irradiation of *cis*-Dihydromayurone (1) in 2-Propanol-d_1.—A solution of 0.200 g of **1** in 10 ml of 2-propanol-d_1 (Stohler Isotopes, deuteration on oxygen) (0.097 M) was irradiated for 11 hr using 8-RUL 3000-Å Rayonet lamps. The hydrindanone product was isolated by alumina chromatography and identified as 3a,7,7-trimethyl-7a-(2-deuteriovinyl)-hexahydro-1-indanone (**7**): 0.015 g (8% yield); mol wt 207; nmr 5.65–6.13 (1 H, m, vinylic H), 5.21 (0.5 H, d, J = 11 Hz, terminal vinylic H), 4.90 (0.5 H, d, J = 18 Hz, terminal vinylic H), 2.2 (2 H, m, α H), 1.18, 1.15, 0.92 (9 H, 3 s, methyl H). Except for the vinylic region (4.6–6.2), the nmr spectrum of **7** was identical with that of **2**.

The other photoproducts were not isolated, but, according to glc, the irradiation closely paralleled the undeuterated 2-propanol irradiation. By mass spectroscopy, no deuterium incorporation could be detected in recovered **1**.

***cis*-8,8,9,10-Tetramethyl-2-decalone (5).**—From lithium–ammonia reduction[10] of **1** there was obtained **5**: mp 150–151° recrystallized from hexane; mol wt 208; ir 1702; nmr 1.10, 1.05, 0.88, 0.81 (4 s, methyl H).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.60; H, 11.47.

***trans*-8,8,9,10-Tetramethyl-2-decalone (14).**—From lithium–ammonia reduction[10] of **6** there was obtained **14**: mol wt 208; ir 1705; nmr 1.37, 1.07, 0.81 (3 s, methyl H), 0.92 (d, J = 1 Hz, methyl H).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.67; H, 11.79.

***cis*-9,10-Dimethyl-2-decalone (13).**—From lithium–ammonia reduction[10] of **12** there was obtained **13**, isolated by benzene elution from an alumina (neutral III) chromatogram: mp 132–134° recrystallized from hexane (lit.[11] mp 108–118°); mol wt 180; ir 1705; nmr 1.04, 0.90 (2 s, methyl H) (lit.[11] nmr 1.05, 0.90).

Registry No.—**1**, 7129-16-0; **2**, 35342-07-5; **3**, 35342-08-6; ***cis*-4**, 35342-09-7; ***trans*-4**, 35342-10-0; **5**, 35342-11-1; **6**, 31090-36-5; **8**, 35342-13-3; **9**, 35342-14-4; **12**, 35340-22-8; **13**, 5523-99-9; **14**, 35340-24-0; 1,9-methano-2-(1-hydroxy-1-methylethyl)-10-methyl-2-decalol, 35340-25-1.

Acknowledgments.—The author would like to thank W. G. Dauben and A. R. Hochstetler for helpful discussions regarding this research and J. Fischer for excellent technical assistance.

(10) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(11) J. A. Marshall, W. I. Fanta, and H. Roebke, *ibid.*, **31**, 1016 (1966).

Sterically Controlled Syntheses of Optically Active Organic Compounds. XV. Syntheses of Optically Active Aspartic Acid through β-Lactam[1]

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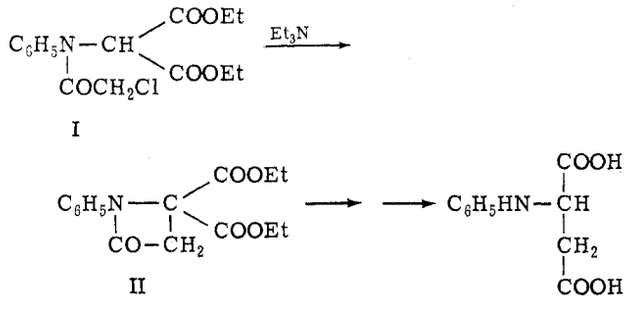
Received September 27, 1971

Optically active *N*-alkyl-*N*-chloroacetamidoacetonitriles were prepared and were converted to their corresponding β-lactams by treatment with sodium hydride. The β-lactams were hydrolyzed and hydrogenolyzed to form optically active aspartic acid. When (*R*)-α-alkylbenzylamines were used, (*S*)-aspartic acid was the result. The yield of aspartic acid from aminoacetonitriles ranged from 36 to 96%. The optical purity of aspartic acid ranged from 21 to 67%. A temperature effect on the sterically controlled reaction was examined. The effect of temperature on the optical purity and yield was found to be small. To examine whether the sterically controlled reaction is due to an asymmetric induction or to a first-order asymmetric transformation, equilibration reactions were carried out using three solvents (dioxane, benzene, acetonitrile). The results indicate that the formation of optically active aspartic acid is largely due to an asymmetric induction.

The cyclization of diethyl *N*-phenyl-*N*-chloroacetamidomalonate (I) to β-lactam (II) has been reported by Sheehan and Bose.[2] Hydrolysis and decarboxylation of the β-lactam yielded *N*-phenylaspartic acid (III).



I

II

III

This reaction is similar to that of cyclization of diethyl ω-bromopropylmalonate in the presence of sodium ethoxide.[3] Several similar β-lactam formations have been recorded.[4–6] Recently, Martin, *et al.*,[7] reported the synthesis of *N*,2-diphenylaspartic acid in a similar way from β-lactam that was formed by cyclization of *N*-chloroacetyl-*N*,2-diphenylglycine ethyl ester. The preparation of β-lactams is summarized in a review by Sheehan and Corey.[8]

In the present study, the β-lactams were prepared from *N*-alkyl-*N*-chloroacetamidoacetonitriles by the cyclization reaction. Hydrolysis and subsequent hydrogenolysis of the β-lactams yielded aspartic acid. When the *N*-alkyl groups were chiral, optically active aspartic acid was obtained. The reaction scheme of this study is shown in Scheme I.

The optically active moieties used were (a) racemic α-

(1) Contribution no. 198 of the Institute for Molecular and Cellular Evolution, University of Miami. Part XIV: K. Harada and K. Matsumoto, *Bull. Chem. Soc. Jap.*, **44**, 1068 (1971).

(2) J. C. Sheehan and A. K. Bose, *J. Amer. Chem. Soc.*, **72**, 5158(1950).

(3) H. M. Walborsky, *ibid.*, **71**, 2941 (1949).

(4) J. C. Sheehan and A. K. Bose, *ibid.*, **73**, 1261 (1951).

(5) A. K. Bose, B. N. Ghosh-Mazumdar, and B. G. Chatterjee, *ibid.*, **82**, 2382 (1960).

(6) B. G. Chatterjee, V. V. Rao, and B. N. Ghosh-Mazumdar, *J. Org. Chem.*, **30**, 4101 (1965).

(7) T. A. Martin, W. T. Comer, C. M. Combs, and J. R. Corrigan, *ibid.*, **35**, 3814 (1970).

(8) J. C. Sheehan and E. J. Corey, *Org. React.*, **9**, 388 (1957).

TABLE I

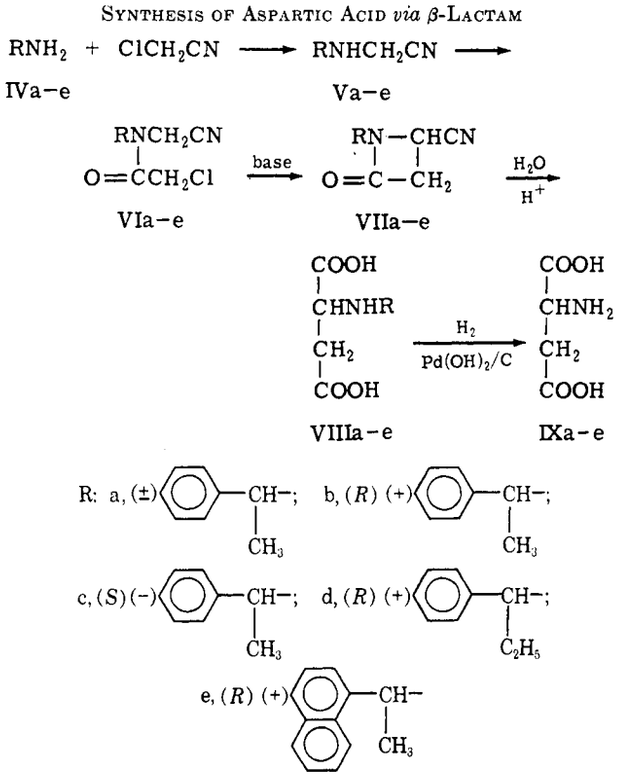
N-ALKYLAMINOACETONITRILES AND THEIR HYDROCHLORIDES[a]

Compd no.	$[\alpha]^{25}D$[b] (benzene)	Bp, °C (mm)	Yield, %	Hydrochloride $[\alpha]^{25}D$[b] (H_2O)	Mp, °C	Formula	Calcd (found), % C	H	N
Va		118–119 (3.0)	64		181–182 dec	$C_{10}H_{12}N_2 \cdot HCl$	61.06 (61.25)	6.66 (6.76)	14.24 (14.13)
Vb	+238.8 (*c* 5.3)	112 (2.2)	50	+50.9 (*c* 1.4)	184–185 dec	$C_{10}H_{12}N_2 \cdot HCl$	61.06 (60.89)	6.66 (6.59)	14.24 (13.84)
Vc	−248.8 (*c* 4.7)	112 (2.2)	51	−50.7 (*c* 2.0)	184–185 dec	$C_{10}H_{12}N_2 \cdot HCl$	61.06 (61.09)	6.66 (6.69)	14.24 (14.23)
Vd	+218.4 (*c* 5.3)	109–110 (0.8)	53	+41.6 (*c* 1.9)	154–155 dec	$C_{11}H_{14}N_2 \cdot HCl$	62.70 (62.98)	7.18 (7.18)	13.30 (13.26)
Ve	+201.4 (*c* 4.9)	163–165 (1.2)	44	−44.4 (*c* 1.3)	200–201 dec	$C_{14}H_{14}N_2 \cdot HCl$	68.15 (68.05)	6.13 (6.17)	11.35 (11.14)

[a] Optically active amines used were (*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 ($[\alpha]^{25}D$ +88.0°, benzene). [b] The specific rotations were measured by the use of JASCO-ORD/UV-5 optical rotatory dispersion recorder using a 10-mm cell.

SCHEME I

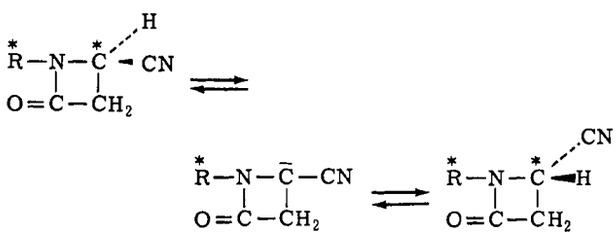
SYNTHESIS OF ASPARTIC ACID *via* β-LACTAM



methylbenzylamine, (b) (*R*)(+)-α-methylbenzylamine, (c) (*S*)(−)-α-methylbenzylamine, (d) (*R*)(+)-α-ethylbenzylamine, and (e) (*R*)(+)-α-(1-naphthyl)-ethylamine. The *N*-alkylaminoacetonitriles Va-e were prepared from amines IVa–e and chloroacetonitrile. The yields and physical properties of Va–e are summarized in Table I. These free *N*-alkylaminonitriles have a large optical rotatory power even at the D line. The melting points, specific rotations, and elemental analyses of these aminonitrile hydrochlorides are also listed in Table I. The aminonitriles were acylated with chloroacetic anhydride to form the *N*-alkyl-*N*-chloroacetamidoacetonitriles (VIa-e). The yields, physical properties, and elemental analyses of the *N*-chloroacetylated aminoacetonitriles (VIa–e) are summarized in Table II.

Acylated *N*-alkylaminoacetonitriles (VIa–e) were treated with sodium hydride in dioxane at various temperatures (25, 50, 75°) to form corresponding β-lactams (VIIa-e). The intermediate lactam VIIa was isolated by distillation and was analyzed for elemental composition. This shows that the lactam is a rather stable compound. The lactam VIIa was hydrolyzed with hydrochloric acid and *N*-α-methylbenzyl-(±)-aspartic acid (VIIIa) was isolated. In the synthesis of optically active aspartic acid, the resulting β-lactams were hydrolyzed with 6 *N* hydrochloric acid without isolation. The resulting *N*-alkylaspartic acids (VIIIa–e) were isolated by the use of a Dowex 50 column and were then hydrogenolyzed using palladium hydroxide on charcoal to yield aspartic acid (IX). The yields of the synthesized aspartic acid are rather high (70 ~ 95%) and the optical purities ranged from 21 to 67%. When (*R*)(+)- and (*S*)(−)-amines were used, (*S*)- and (*R*)-aspartic acids were formed. When α-methylbenzylamine was used, the optical purity of aspartic acid ranged from 41 to 49%. The use of α-ethylbenzylamine resulted in a decrease in the optical purity (19–29%). However, when α-(1-naphthyl)ethylamine was used, the optical purity of the resulting aspartic acid increased considerably (54–67%). The temperature effect on the asymmetric synthesis results in a rather small change in the yield and also in optical activity of the resulting aspartic acid. However, the optical purities of aspartic acid prepared at 50° seemed a little higher than those of aspartic acid prepared at 25 and 75°. The results are summarized in Table III.

Few asymmetric syntheses of four-membered carbocyclic or heterocyclic ring systems have been reported[9] and it was important to establish that asymmetric induction occurred during ring closure rather than by epimerization of the α-carbon atom. To examine the possibility of the formation of optically active aspartic acid by asymmetric transformation, three different solvents (dioxane, benzene, and acetonitrile) were used



(9) L. A. Paquette and J. P. Freeman, *J. Amer. Chem. Soc.*, **91**, 7548 (1969), have reported the asymmetric synthesis of a thiete 1,1-dioxide.

TABLE II

N-ALKYL-*N*-CHLOROACETAMIDOACETONITRILES

Compd no.	$[\alpha]^{25}D$[a] (dioxane)	Bp (mm) or mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
VIa		184–185 (1.5)	89	$C_{12}H_{13}N_2OCl$	60.89	5.54	11.84	61.09	5.46	11.87
VIb	+95.0 (*c* 1.9)	91–92	87	$C_{12}H_{13}N_2OCl$	60.89	5.54	11.84	60.60	5.71	11.74
VIc	−95.8 (*c* 1.5)	91–92	89	$C_{12}H_{13}N_2OCl$	60.89	5.54	11.84	60.71	5.63	11.69
VId	+129.5 (*c* 2.7)	183–184 (1.9)	79	$C_{13}H_{15}N_2OCl$	62.55	6.09	10.85	62.29	6.03	11.17
VIe	+60.2 (*c* 1.7)	92–94	82	$C_{16}H_{15}N_2OCl$	67.26	5.29	9.77	67.01	5.26	9.80

[a] The specific rotations were measured by the use of a JASCO ORD/UV-5 optical rotatory dispersion recorder using a 10-mm cell.

TABLE III

SYNTHESIS OF OPTICALLY ACTIVE ASPARTIC ACID

Starting material[a]	Confign of asymmetric moiety[b]	Temp, °C	Time, hr	Confign	Aspartic acid yield, %[c]	DNP-aspartic acid, $[\alpha]^{25}D$ (1 *N* NaOH)[d]	Optical purity, %[e]
VIa	±	25	12	±	36		
	±	25	36	±	92		
	±	50	5	±	94		
VIb	(*R*)(+)-Me	25	36	*S*	96	+39.8 (*c* 1.7)	43
	(*R*)(+)-Me	50	5	*S*	54	+42.8 (*c* 1.5)	47
	(*R*)(+)-Me	75	5	*S*	75	+41.3 (*c* 1.5)	45
VIc	(*S*)(−)-Me	25	36	*R*	75	−37.7 (*c* 1.7)	41
	(*S*)(−)-Me	50	5	*R*	72	−44.8 (*c* 1.6)	49
	(*S*)(−)-Me	75	5	*R*	44	−40.7 (*c* 1.4)	44
VId	(*R*)(+)-Et	25	36	*S*	76	+19.4 (*c* 1.5)	21
	(*R*)(+)-Et	50	5	*S*	67	+28.9 (*c* 1.5)	31
	(*R*)(+)-Et	75	5	*S*	75	+26.8 (*c* 1.5)	29
Ve	(*R*)(+)-Naph	25	36	*S*	69	+58.7 (*c* 1.4)	64
	(*R*)(+)-Naph	50	5	*S*	75	+62.0 (*c* 1.6)	67
	(*R*)(+)-Naph	75	5	*S*	68	+49.3 (*c* 1.6)	54

[a] In each reaction, 0.0025 mol of VI and 0.0025 mol of sodium hydride in 20 ml of dioxane were used. [b] (*R*)(+)-Me, (*R*)(+)-α-methylbenzylamine ($[\alpha]^{25}D$ +41.5°, benzene); (*S*)(−)-Me, (*S*)(−)-α-methylbenzylamine ($[\alpha]^{25}D$ −42.3°, benzene); (*R*)(+)-Et, (*R*)(+)-α-ethylbenzylamine ($[\alpha]^{25}D$ +21.7°, benzene); (*R*)(+)-Naph, (*R*)(+)-α-(1-naphthyl)ethylamine ($[\alpha]^{25}D$ +88.0°, benzene). [c] The yields were calculated from the data obtained from an amino acid analyzer and are based on the starting N,N-disubstituted aminoacetonitriles (VIa–e). [d] The specific rotations were measured by the use of a JASCO ORD/UV-5 optical rotatory dispersion recorder using a 10-mm cell. [e] The optical purity is defined as $[\alpha]D^{obsd}/[\alpha]D^{lit.} \times 100$. DNP-(*S*)-aspartic acid, $[\alpha]^{25}D$ +91.9° (1 *N* NaOH).

to detect the epimerization process. After normal β-lactam formation using dioxane and sodium hydride, the reaction mixture was divided into three parts. The first part was kept standing at room temperature under agitation for 24 hr; the other two parts were evaporated almost to dryness under reduced pressure. To these residues, benzene and acetonitrile were added and the mixtures were kept standing under agitation for 24 hr at room temperature. If first-order asymmetric transformation took place during the agitation in these different solvents, the optical purities of the resulting aspartic acid would be expected to be different. The results are summarized in Table IV.

TABLE IV

OPTICAL PURITIES OF DNP-ASPARTIC ACID PREPARED BY EQUILIBRATION IN VARIOUS SOLVENTS

Solvent	Dielectric constant	$[\alpha]^{25}D$ (*c* 1.6–1.9, 1 *N* NaOH)[a]	Optical purity, %[a]
Dioxane	2.2	+38.0 (+37.9)	41.4 (40.8)
CH_3CN	37.5	+34.3 (+34.2)	37.4 (37.2)
Benzene	2.3	+35.2 (+33.6)	38.5 (36.6)

[a] The values in parentheses are results obtained in the repeated experiment.

The results show that the optical purities of aspartic acid in various solvents are similar; however, the value obtained using dioxane seems a little higher than those obtained by the use of benzene and acetonitrile. This slight difference might be due to experimental error or epimerization during the equilibration. However, the values obtained by the use of benzene (ε 2.27) and acetonitrile (37.5) are almost the same. If the equilibration in acetonitrile took place, the optical purity of the aspartic acid would be expected to be different from those obtained by the use of dioxane and benzene. Therefore, the equilibration reactions suggest that the effect of first-order asymmetric transformation is not great and that the optical activity of aspartic acid is largely due to asymmetric induction during the lactam formation.

It is of crucial importance in sterically controlled syntheses to measure optical activities of the product without any fractionation of the optical isomers. The ion-exchange separation of the synthesized amino acid is a preferred technique of isolation. However, the method usually does not give chemically pure amino acids. Therefore, further purification without fractionation of optical isomers is usually necessary. In the present work, all amino acids isolated by ion exchange were dinitrophenylated by the use of 2,4-dinitrofluorobenzene.[10,11] The resulting DNP-amino acids were

(10) F. Sanger, *Biochem. J.*, **39**, 507 (1945).
(11) K. R. Rao and H. A. Sober, *J. Amer. Chem. Soc.*, **76**, 1328 (1954).

chromatographically purified[12] and isolated without fractionation of the optical isomers.[13]

Experimental Section

[N-(S)(−)-α-Methylbenzyl]aminoacetonitrile (Vc).—(S)(−)-α-Methylbenzylamine (12.1 g, 0.10 mol), triethylamine (10.1 g, 0.10 mol), and chloroacetonitrile (7.6 g, 0.10 mol) were dissolved in 60 ml of absolute alcohol. The solution was refluxed gently for 4 hr in an oil bath. After the reaction was over, the ethanol was evaporated *in vacuo*. The residue was dissolved in 100 ml of ethyl acetate and the solution was washed with water. The solution was dried with anhydrous sodium sulfate and the solvent was evaporated. The residual oil was distilled under reduced pressure: bp 121° (2.2 mm); yield, 8.23 g (51.4%); $[\alpha]^{25}D$ −248.8° (*c* 4.7, benzene).

Other *N*-alkylaminonitriles were prepared in a similar way. The yields and physical properties of the free *N*-alkyl-aminonitriles (Va–e) and the physical properties and elemental analyses of their hydrochlorides are summarized in Table I.

***N*-(S)(−)-α-Methylbenzyl-*N*-chloroacetamidoacetonitrile (VIc).**—Vc (8.0 g, 0.05 mol) was dissolved in 120 ml of dry benzene. To this solution, chloroacetic anhydride, 8.6 g (0.05 mol) was added slowly. The solution was then refluxed for 3 hr in an oil bath. After the reaction was over, the benzene solution was washed with 0.1 *N* hydrochloric acid, 3% sodium hydrogen carbonate, and water. The benzene solution was dried with anhydrous sodium sulfate and the solvent was evaporated. The residual crystals were recrystallized from ethanol: yield, 10.5 g (88.5%); mp 91–92°; $[\alpha]^{25}D$ −95.8° (*c* 1.5, dioxane). Elemental analyses are shown in Table II.

Other *N*-alkyl-*N*-chloroacetamidoacetonitriles were prepared in a similar way. The physical properties, yields, and elemental analyses are shown in Table II.

(R)-Aspartic Acid (IXc).—Sodium hydride (0.10 g, 0.0025 mol, 60% suspension in mineral oil) was suspended in 30 ml of anhydrous dioxane. To this mixture, 0.59 g (0.0025 mol) of VIc in 20 ml of anhydrous dioxane was added slowly at room temperature for a period of 2 hr under agitation. After the addition was over, the reaction mixture was stirred for 34 hr. In the cyclization reactions (VI → VII) at 50 and at 75°, the reaction mixtures were stirred for 3 hr at the temperatures after the addition of VI was over. The precipitated salt was then removed by filtration and the solvent was evaporated under reduced pressure. The residue was hydrolyzed with 50 ml of 6 *N* hydrochloric acid for 6 hr. The solution was extracted twice with ether, and the aqueous solution was evaporated to dryness *in vacuo*. The residue was dissolved in a small amount of water and the solution was applied to a Dowex 50 column (H^+ form, 1.9 cm × 23 cm). The column was eluted with 1.5 *N* aqueous ammonia and the fractions containing amino acid were combined and evaporated under reduced pressure. The residual product (VIIIc) was dissolved in water and was hydrogenolyzed by the use of 0.5 g of palladium hydroxide on charcoal for 12 hr. After the reaction was over, the catalyst was removed by filtration. A part of the solution was diluted in a proper way, and was analyzed on an automatic amino acid analyzer to determine accurately the yield of aspartic acid. Aspartic acid (IXc) was obtained by evaporation of the water. The yield of aspartic acid was found to be 74.9%. A part of the aspartic acid was recrystallized from water and ethanol for elemental analysis. Calcd: N, 10.52. Found: N, 10.40. The rest of the aspartic acid was converted to DNP-aspartic acid in the usual way, and the resulting DNP-aspartic acid was purified by the use of a Celite column treated with a pH 4 citrate–phosphate buffer.[10,11] DNP-(*R*)-aspartic acid had $[\alpha]^{25}D$ −37.7° (*c* 1.7, 1 *N* NaOH); optical purity, 41%.

(12) J. C. Perrone, *Nature* (London), **167**, 513 (1951).

(13) K. Harada and K. Matsumoto, *J. Org. Chem.*, **32**, 1794 (1967).

Isolation of (±)-Lactam (VIIa).—Sodium hydride (60%, 0.40 g, 0.01 mol) was suspended in 50 ml of anhydrous dioxane. To this suspension, 2.36 g (0.01 mol) of VIa in 20 ml of anhydrous dioxane was added dropwise at room temperature under agitation over a period of 2 hr. After the addition was over, the reaction mixture was stirred at room temperature for an additional 36 hr. The solvent was then removed under reduced pressure. The residue was dissolved in 50 ml of ethyl acetate and the solution was washed with 30 ml of 1 *N* hydrochloric acid, with 2% sodium hydrogen carbonate, and then with water. The ethyl acetate solution was dried with anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the residual oil was distilled under reduced pressure and VIIa, 1.40 g (70%), was obtained, bp 151–152° (1.5 mm).

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04. Found: C, 71.94; H, 6.61.

N-α-Methylbenzyl-(±)-aspartic Acid (VIIIa).—Lactam VIIa (0.8 g, 0.004 mol) was refluxed with 20 ml of 6 *N* hydrochloric acid for 6 hr. The hydrolysate was extracted with ether to remove colored material and the aqueous solution was evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water and the solution was applied to a Dowex 50 column (hydrogen form) and was eluted with 1 *N* aqueous ammonia. The fractions containing the amino acid were combined and evaporated under reduced pressure. The pH of the concentrated aqueous solution was adjusted to about 2.8; *N*-alkylaspartic acid (VIIIa) crystallized. Then VIIIa was recrystallized from water–alcohol; VIIIa, 0.75 g (73%), was obtained, mp 181–183° dec.

Anal. Calcd for $C_{12}H_{15}NO_4 \cdot H_2O$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.71; H, 6.84; N, 5.65.

Equilibration Reaction of Lactam VIIb Using Various Solvents.—Sodium hydride (60%, 0.3 g, 0.0075 mol) was suspended in 80 ml of anhydrous dioxane. To this, 1.78 g (0.0075 mol) of VIb in 30 ml of absolute dioxane was added dropwise in the manner described above. The reaction mixture was stirred for 36 hr. The reaction mixture was then divided equally into three portions. A dioxane portion was kept at room temperature for an additional 24 hr under agitation. The other two portions were evaporated to dryness under reduced pressure avoiding contamination by moisture. To one of the dried residues, 35 ml of dry benzene was added, and, to the other residue, 35 ml of acetonitrile was added. These solutions were then kept at room temperature for 24 hr under agitation. The three reaction mixtures were then evaporated under reduced pressure. As described earlier, the residues were then hydrolyzed and hydrogenolyzed to yield optically active aspartic acid. The specific rotations and optical purities of DNP-aspartic acid obtained by the use of various solvents are summarized in Table IV.

Registry No.—Va, 35341-72-1; Va HCl, 35341-73-2 Vb, 35341-74-3; Vb HCl, 35341-75-4; Vc, 35341-76-5; Vc HCl, 35341-77-6; Vd, 35341-78-7; Vd HCl, 35341-79-8; Ve, 35341-80-1; Ve HCl, 35341-81-2; VIa, 35341-82-3; VIb, 35341-83-4; VIc, 35341-84-5; VId, 35341-85-6; VIe, 35341-86-7; VIIa, 35341-87-8; VIIIa, 17196-56-4; (*R*)-aspartic acid, 1783-96-6; (*S*)-aspartic acid, 56-84-8; DNP-(*R*)-aspartic acid, 7690-55-3.

Acknowledgments.—This work was supported by Grant No. NGR 10-007-052 of the National Aeronautics and Space Administration. The authors wish to express their thanks to Dr. Kazuo Matsumoto for valuable discussions and to Mr. Charles R. Windsor for amino acid analyses.