equivalents), and acrylonitrile 104 mg (3 equivalents) were dissolved in DMF 4 ml. The mixture was sealed in a quartz glass tube and irradiated with Toshiba Lamp SHL-100 UD at *ca.* 1 cm distance for 24 hr. The temperature of reaction mixture elevated to 80–90° by radiant heat. The reaction mixture diluted with water (150 ml) was extracted with ether, and insoluble materials were filtered off. Ether in water layer was evaporated *in vacuo*. The desalted solution (T.O.D._{248.5} 6500) was applied to the column of Dowex 1×8 (Cl form, 100–200 mesh, 2×8 cm, 25 ml) and washed with water. The nucleotides were eluted in a stepwise manner as follows. Hypoxanthine and isopropylidene inosine with water (Fraction I, T.O.D._{248.5} 3300, 54% of the total eluate optical density unit.), isopropylidene 5'-IMP with 0.01 N HCl+0.03 M NaCl (Fraction II, T.O.D._{248.5} 2570, 42%), and isopropylidene 5'-IDP with 0.1 N HCl (Fraction III, T.O.D._{248.5} 190, 3%). The recovery estimated from T.O.D. applied to the column was 94%.

Desalted Fraction II was concentrated to a small volume, adjusted to pH 1.5 with aqueous hydrochloric acid solution and warmed for 20 min at 70°, and desalted with charcoal. The concentrated eluate was passed through a column of IR-120 (Na form, 9 ml) to convert ammonium salt to sodium salt. After concentration to dryness, the residue was recrystallized from H₂O-EtOH to give 60 mg 5'-IMP·Na₂, (purity estimated spectrophotometrically on the weight basis 88.3%). UV: $\lambda_{\text{max}}^{0.1N \text{ HCl}}$ 248.5 m μ ; $\lambda_{\text{max}}^{0.1N \text{ NaOH}}$ 252.5 m μ . This sample was identical with 5'-IMP by paper electrophoresis and NMR.

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Chemistry of Amino Acids. VI.¹⁾ Studies on α -Alkyl- α -amino Acids. X.¹⁾ Unusual Alkyl Migration in the Hofmann Degradation of 5-(2-Dialkylaminoethyl)-5-methylhydantoin Quarternary Ammonium Hydroxide Anhydronium Base

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Previously the chemical correlation of the absolute configuration of (+)- α -methylserine, one of the optically active α -alkyl- α -amino acids from a natural source, with S(+)-isovaline, was reported from our laboratory.³⁾ In this study, 5-methyl-5-vinylhydantoin (I) was selected as a key intermediate and obtained successfully from the thermal decomposition of 5-(2-dimethylaminoethyl)-5-methylhydantoin N-oxide (II). Before this, several unsuccessful attempts to obtain I were undertaken, one of which was the Hofmann degradation of 5-(2-dialkylaminoethyl)-5-methylhydantoin quarternary ammonium hydroxide anhydronium base (IIIa, and IIIb). In this case, instead of the objective hydantoin (I), 3-alkyl-hydantoin (IVa, and IVb) was obtained in a fairly good yield by the unexpected alkyl migration from the side chain nitrogen to the 3-position of the hydantoin ring.

The materials used in the Hofmann degradation, IIIa and IIIb, were prepared as follows: 5-(2-dimethylaminoethyl)-5-methylhydantoin (Va), prepared from 1-dimethylamino-3-butanone (VIa)³⁾ using the Bücherer reaction in a 59% yield,³⁾ was treated with methyl iodide to afford 5-(2-dimethylaminoethyl)-5-methylhydantoin methiodide (VIIa) quantitatively. This product was applied to an ion exchange resin column (Amberlite IRA-400 (OH⁻ form)),

1) Part V, Part IX: K. Hiroi, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16**, 444 (1968).

2) Location: *Hongo, Tokyo*.

3) N. Takamura, S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **15**, 1776 (1967).

and the eluates and water washings gave 5-(2-dimethylaminoethyl)-5-methylhydantoin methohydroxide anhydronium base (IIIa) in a quantitative yield. The infrared spectrum of IIIa showed two carbonyl bands at unusually lower wave numbers (IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1685, 1587) than those of the parent hydantoin (VIIa) (IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1777, 1714). This was probably due to the fact that in a solid state IIIa does not involve a normal quaternary ammonium hydroxide structure (X) but involves an anhydronium base form (III), in which the resonance stabilization as shown in the structure of III⁴) should occur. Further support for the above conclusion was obtained from the observations that sodium salt (XI), prepared from Va and sodium hydride in dioxane, also showed two carbonyl bands at 1692 and 1585 cm^{-1} , and that IIIa was easily reconverted to VIIa after treatment with hydriodic acid.

Thus, the IIIa obtained was heated *in vacuo* under a nitrogen atmosphere⁵⁾ to give 5-(2-dimethylaminoethyl)-3,5-dimethylhydantoin (IVa) in a 72% yield, whose structure was confirmed from its elemental analysis, and its infrared (IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1772, 1713) and nuclear magne-

4) J.D. Roberts and M.C. Caserio, "Basic Principles of Organic Chemistry," W.A. Benjamin, Inc., 1964, pp. 232-242.

tic resonance spectra (three singlets at 8.60τ ($3H$, $-\underline{C}-\underline{CH}_3$), 7.83τ ($6H$, $(\underline{CH}_3)_2N-$), and 7.02τ ($3H$, $>N-\underline{CH}_3$)). IVa afforded its methiodide (IXa) in a good yield as usual.⁶⁾ Hydrolysis of IVa with barium hydroxide^{7,8)} under reflux for 50 hr gave 2-amino-2-methyl-4-dimethylamino-butyric acid (VIIIa), which was identical with that prepared alternatively from Va. These results evidently show that a methyl group migrated from the nitrogen in the side chain to the 3-position of the hydantoin ring.⁹⁾

Similar alkyl migration was observed for the ethyl group. 5-(2-Diethylaminoethyl)-5-methylhydantoin (Vb) prepared from 1-diethylamino-3-butanone (VIb)¹⁰⁾ was converted to its ethiodide (VIIb) in a 58% yield. The VIIb obtained was treated with ion exchange resin (Amberlite IRA-400 (OH^- form)), as before, to give quarternary ammonium anhydronium base (IIIb), which in this case without separation, was submitted to thermal migration *in vacuo* under a nitrogen atmosphere to afford 5-(2-diethylaminoethyl)-3-ethyl-5-methylhydantoin (IVb) as a colorless oil in a 52% yield from VIIb. IVb was also identified as its methiodide (IXb).

Next, intermolecular N-alkylation to the 3-position of the hydantoin ring using tetra-alkylammonium hydroxide as an alkylating agent was undertaken, since in the above alkyl migration reactions the quarternary ammonium part of the anhydronium base seemed to act as an intra or intermolecular alkylating agent.¹¹⁾ In fact, the mixture of Va and tetramethylammonium hydroxide was heated *in vacuo* under a nitrogen atmosphere to give IVa in a 85% yield. IVb was similarly obtained in a 75% yield using Vb and tetraethylammonium hydroxide.

XII

The reasons why a normal Hofmann degradation had not been observed in IIIa and IIIb are obscure. But difficulties from steric hindrance in forming the trans conformation as shown in XII, which should be in a normal Hofmann degradation,⁵⁾ might account for the above unusual migration.

5) A.C. Cope, *Org. Reac.*, **11**, 317 (1960).

6) An attempt to prepare an olefinic compound from IXa through its hydroxide was also unsuccessful.

7) S.D. Upham and O.C. Dermer, *J. Org. Chem.*, **22**, 799 (1957).

8) K.T. Potts, *J. Chem. Soc.*, **1955**, 1632.

9) A similar and unusual alkylation on nitrogen in the Hofmann degradation was reported with some oxyindole alkaloid methohydroxides (see ref. 5, p. 355).

10) A.L. Wilds and C.H. Shunk, *J. Am. Chem. Soc.*, **65**, 469 (1943).

11) Intermolecular N-alkylation using tetra-alkylammonium hydroxide as an alkylating agent was observed in the adenine series (T.C. Myers and L. Zeleznick, *J. Org. Chem.*, **28**, 2087 (1963)).

Experimental¹²⁾

5-(2-Dimethylaminoethyl)-5-methylhydantoin (Va) and Its Methiodide (VIIa)—Va was obtained from 1-dimethylamino-3-butanone (VIa),³⁾ as reported previously, in a 59% yield, mp 181° (lit.,³⁾ mp 181°).

NMR¹³⁾: +217 (3H, singlet, $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), +179 $\left(2\text{H, triplet, } J=8 \text{ cps, } \text{CH}_2-\overset{\text{H}_3\text{C}}{\underset{|}{\text{C}}}-\right)$, +139 (6H, singlet, $(\text{CH}_3)_2\text{N}-\text{CH}_2-$).

VIIa was prepared from Va using methyl iodide in ethanol in the usual quantitative yield, mp 254° (decomp.). Pure VIIa was obtained as colorless crystals after several recrystallizations from EtOH-H₂O, mp 259° (decomp.). Anal. Calcd. for C₉H₁₈O₂N₃I: C, 33.04; H, 5.54; N, 12.85. Found: C, 33.17; H, 5.28;

N, 12.27. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3160, 1777, 1714, 1194. NMR¹³⁾: +200 (3H, singlet, $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), +152 $\left(2\text{H, triplet, } J=8 \text{ cps, } \text{CH}_2-\overset{\text{H}_3\text{C}}{\underset{|}{\text{C}}}-\right)$, +101 (9H, singlet, $(\text{CH}_3)_3\text{N}^+$). The signal of the CH₂ group adjacent to $(\text{CH}_3)_3\text{N}^+$ was superimposed with that of $(\text{CH}_3)_3\text{N}^+$ group.

1-Diethylamino-3-butanone (VIb)—VIb was prepared using the method reported by Wilds, *et al.*¹⁰⁾ in a 65% yield. bp 75—76.5° (18 mmHg) (lit.,¹⁰⁾ bp 70—70.5° (11 mmHg)).

5-(2-Diethylaminoethyl)-5-methylhydantoin (Vb) and Its Ethiodide (VIIb)—A mixture of VIb (18.0 g, 0.126 mole), KCN (95% pure) (10.3 g, 0.151 mole) and (NH₄)₂CO₃ (39.9 g, 0.416 mole) in 50 v/v% aq. EtOH (200 ml) was stirred at 55° for 10 hr, and then at 80—90° for 40 min. The pale yellow reaction mixture was evaporated to dryness *in vacuo* to give a mixture of viscous oil and crystals, to which was added EtOH (200 ml). Refluxing for 30 min, filtration, and then evaporation to dryness afforded a reddish brown oil, which was purified with a silica gel column (600 g, solvent acetone) to give crude Vb as yellow crystals (13.0 g, 48%), mp 112—117°. Several recrystallizations from EtOAc gave pure Vb as colorless prisms, mp 124°. Anal. Calcd. for C₁₀H₁₉O₂N₃: C, 56.31; H, 8.98; N, 19.70. Found: C, 56.45; H, 8.54; N, 19.84. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 2970, 1772, 1712, 1406, 1197, 761. NMR¹³⁾: +213 (6H, triplet, $J=7 \text{ cps, } (\text{CH}_3\text{CH}_2)_2\text{N}-$), +204 (3H, singlet, $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), +166 $\left(2\text{H, triplet, } J=8 \text{ cps, } \text{CH}_2-\overset{\text{H}_3\text{C}}{\underset{|}{\text{C}}}-\right)$, +126—+81 (6H, multiplet, $(\text{CH}_3\text{CH}_2)_2\text{N}-\text{CH}_2-$).

VIIb was obtained from Vb under reflux with ethyl iodide in ethanol in a 58% yield, mp 227° (decomp.). Several recrystallizations from EtOH-H₂O gave pure VIIb as colorless prisms, mp 235° (decomp.). Anal. Calcd. for C₁₂H₂₄O₂N₃I: C, 39.03; H, 6.55; N, 11.38. Found: C, 38.84; H, 6.53; N, 11.43. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3215, 1771, 1715, 1406, 1019. NMR¹³⁾: +208 (9H, triplet, $J=7 \text{ cps, } (\text{CH}_3\text{CH}_2)_3\text{NCH}_2-$), +192 (3H, singlet, $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), +151 $\left(2\text{H, triplet, } J=8 \text{ cps, } \text{CH}_2-\overset{\text{H}_3\text{C}}{\underset{|}{\text{C}}}-\right)$, +107—+68 (8H, multiplet, $(\text{CH}_3\text{CH}_2)_3\text{N}^+\text{CH}_2-$).

5-(2-Dimethylaminoethyl)-5-methylhydantoin Methohydroxide Anhydronium Base (IIIa)—VIIa (1.0 g, 0.003 mole) was dissolved in a small amount of H₂O, and passed through an ion exchange resin column (Amberlite IRA-400 (OH⁻ form, 30 ml)). The column was washed with H₂O and the alkaline eluate was collected and evaporated to dryness *in vacuo* to afford IIIa as colorless crystals (0.76 g, quantitative yield), mp 232—233° (decomp.). Several recrystallizations from H₂O-EtOH-ether gave pure IIIa as colorless crystals, mp 260° (decomp.). Anal. Calcd. for C₉H₁₇O₂N₃·2H₂O: C, 45.94; H, 9.00; N, 17.86. Found: C, 45.71; H, 8.93; N, 17.90. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400 (broad), 1685, 1587, 1385, 1366. NMR¹³⁾: +209 (3H, singlet, $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), +164 $\left(2\text{H, triplet, } J=8 \text{ cps, } \text{CH}_2-\overset{\text{H}_3\text{C}}{\underset{|}{\text{C}}}-\right)$, +106 (9H, singlet, $(\text{CH}_3)_3\text{N}^+$). The signal of the CH₂ group adjacent to $(\text{CH}_3)_3\text{N}^+$ was superimposed with that of $(\text{CH}_3)_3\text{N}^+$ group.

IIIa (0.22 g) obtained above, was dissolved in diluted hydriodic acid solution (57% HI (0.3 ml) and H₂O (4 ml)), and the whole was evaporated to dryness *in vacuo* to afford VIIa as colorless crystals (0.23 g), mp 257.5° (decomp.). Infrared spectrum of VIIa thus prepared was identical with that of the authentic sample, and the mixed melting point with the authentic VIIa showed no depression.

5-(2-Dimethylaminoethyl)-3,5-dimethylhydantoin (IVa)—a) IVa from IIIa: Crude IIIa, prepared from VIIa (3.27 g, 0.01 mole) as colorless crystals was, without further purification gradually heated in distillation flask under reduced pressure (3 mmHg) in N₂ atmosphere. The temperature of the reaction mixture reached,

12) All melting points are uncorrected. IR spectra measurements were performed with a Spectrometer, Model DS-402, Japan Spectroscopic Co., Ltd. NMR spectra were determined with a Spectrometer, Model 3H-60, Japan Electron Optics Lab.

13) Solvent D₂O 60 Mc, cps upperfield from H₂O.

was 200° after 35 min heating, and was kept at 200—210° for 5 hr. The oil distilled from the distillation flask solidified gradually. The crystals obtained was collected with acetone and recrystallized from the same solvent to give crude IVa as pale yellow prisms (1.44 g, 72%), mp 112—113°. Pure IVa was obtained as colorless prisms after several recrystallizations from acetone, mp 114.5°. *Anal.* Calcd. for $C_9H_{17}O_2N_3$: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.49; H, 8.48; N, 21.10. IR $\nu_{\max}^{KBr}$ cm^{-1} : 2980, 1772, 1713, 1446, 1042. NMR (solvent $CDCl_3$, 60 Mc, TMS internal standard): 8.60 τ (3H, singlet, $\overset{\overset{CH_3}{|}}{-C-CH_3}$), 7.83 τ (6H, singlet, $(CH_3)_2N-$), 7.02 τ (3H, singlet, $-CO-\overset{\overset{CH_3}{|}}{N}-CO-$), 7.5—8.4 τ (4H, multiplet, $-NCH_2CH_2-\overset{\overset{CH_3}{|}}{C}-$).

IVa was converted to its methiodide (IXa) as usual, prisms, mp 242—243° (recrystallized from MeOH). *Anal.* Calcd. for $C_{10}H_{20}O_2N_3I$: C, 35.20; H, 5.90; N, 12.31. Found: C, 35.03; H, 5.80; N, 12.27. IR $\nu_{\max}^{KBr}$ cm^{-1} : 3220, 1768, 1704, 1474, 1399. NMR¹³⁾ +195 (3H, singlet, $\overset{\overset{CH_3}{|}}{-C-CH_3}$), +146 (2H, triplet, $J=8.5$ cps, $-CH_2-\overset{\overset{H_3C}{|}}{C}-$), +106 (3H, singlet, $-CO-\overset{\overset{CH_3}{|}}{N}-CO-$), +96 (9H, singlet, $(CH_3)_3N^+$), +79 (2H, triplet, $J=8.5$ cps, $N^+-CH_2CH_2-$).

b) IVa from Va and tetramethylammonium hydroxide: 10% aq. $(CH_3)_4NOH$ solution (10 g, 0.011 mole) containing Va (1.85 g, 0.01 mole) was evaporated to dryness *in vacuo* under a N_2 atmosphere to give wet crystals, which were heated gradually under reduced pressure (5 mmHg) in a N_2 atmosphere until the reaction temperature was reached at 210° after 40 min heating. The temperature was kept at 210—230° for 30 min. The distillate obtained above solidified (1.7 g, 85%), mp 107—112° and was recrystallized from acetone to afford pure IVa, mp 114.5°. Infrared and NMR spectra of IVa thus prepared were identical with those of IVa obtained from IIIa. The mixed melting point with IVa obtained from IIIa showed no depression.

5-(2-Diethylaminoethyl)-3-ethyl-5-methylhydantoin (IVb) and Its Methiodide (IXb)—a) IVb and IXb from VIIb through IIIb: A small amount of H_2O containing VIIb (2.0 g, 0.0054 mole) was poured through an ion exchange column (Amberlite IRA-400 (OH^- form, 30 ml)). The column was eluted with H_2O , and the alkaline eluate was collected and evaporated to dryness *in vacuo* to give IIIb as a colorless oil, which was then submitted to the thermal migration reaction under reduced pressure (10—11 mmHg) in a nitrogen stream. The reaction temperature was raised gradually to 180° for 35 min and kept at 180—190° for 25 min. Pale brown oil left in the reaction flask was purified using Al_2O_3 column chromatography (100 g, solvent, EtOAc) to afford pure IVb as a colorless oil¹⁴⁾ (0.68 g, 52%), IR $\nu_{\max}^{CaF_2}$ cm^{-1} : 3290, 2980, 1775, 1715, 1455, 1064. NMR (solvent, $CDCl_3$, 60 Mc, TMS internal standard): 9.00 τ (6H, triplet, $J=7$ cps, $(CH_3CH_2)_2N-$), 8.79 τ (3H, triplet, $J=7$ cps, $-CO-\overset{\overset{CO}{|}}{N}-CH_2CH_3$), 8.60 τ (3H, singlet, $\overset{\overset{CH_3}{|}}{-C-CH_3}$), 8.40 τ —7.10 τ (8H, multiplet, $(CH_3-CH_2)_2NCH_2CH_2-\overset{\overset{CH_3}{|}}{C}-$), 6.46 τ (2H, quartet, $J=7$ cps, $-CO-\overset{\overset{CO}{|}}{N}-CH_2CH_3$).

Methiodide (IXb) was prepared from IVb as usual and recrystallized from MeOH-ether as colorless needles, mp 168—168.5°. The IXb thus obtained showed no depression in its mixed melting point with the authentic IXb (see b)). Its infrared and NMR spectra were also superimposable with those of the authentic IXb (see b)).

b) IVb and IXb from Vb and tetraethylammonium hydroxide: A 10% aq. Et_4NOH solution (16 g, 0.011 mole) containing Vb (2.13 g, 0.01 mole) was evaporated to dryness *in vacuo* under a N_2 atmosphere to give an oil, which was submitted to the thermal reaction in distillation flask under reduced pressure (5 mmHg). The reaction temperature was raised gradually to 190° for 40 min, and was kept at 190—220° for 40 min. The distillate (1.4 g) solidified and showed a mp of 38—43°. The residue in the reaction flask was purified using Al_2O_3 column chromatography (100 g, solvent EtOAc) to afford more IVb (0.4 g), mp 47—49°. The total yield of IVb was 75%. IR $\nu_{\max}^{KBr}$ cm^{-1} : 3355, 2980, 2800, 1756, 1714. NMR (solvent, $CDCl_3$, 60 Mc, TMS internal standard): 9.00 τ (6H, triplet, $J=7$ cps, $(CH_3CH_2)_2N-$), 8.80 τ (3H, triplet, $J=7$ cps, $-CO-\overset{\overset{CO}{|}}{N}-CH_2CH_3$), 8.61 τ (3H, singlet, $\overset{\overset{CH_3}{|}}{-C-CH_3}$), 8.40 τ —7.10 τ (8H, multiplet, $(CH_3-CH_2)_2NCH_2CH_2-\overset{\overset{CH_3}{|}}{C}-$), 6.45 τ (2H, quartet, $J=7$ cps, $-CO-\overset{\overset{CO}{|}}{N}-CH_2CH_3$). This NMR spectrum was identical with

14) IVb prepared from another synthetic route (see b) was obtained as crystals, but was found to be too difficult to purify by recrystallization.

that of IVb prepared from VIIb. It was too difficult to purify IVb by the recrystallization method,¹⁴ so IVb was identified as its methiodide (IXb), colorless needles (recrystallized from MeOH-ether), mp 167—168°. *Anal.* Calcd. for $C_{13}H_{26}O_2N_3I$: C, 40.74; H, 6.84; N, 10.96. Found: C, 40.77; H, 6.79; N, 11.22.

IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3200, 2985, 1769, 1706, 1447. NMR¹³: +213 (3H, triplet, $J=7$ cps, $-\text{CO}-\text{N}-\text{CH}_2\text{CH}_3$), +206 (6H, triplet, $J=7$ cps, $(\text{CH}_3\text{CH}_2)_2\text{N}^+$), +193 (3H, singlet, $-\text{C}-\text{CH}_3$), +149 (2H, triplet, $J=9$ cps, $-\text{CH}_2-\text{C}-$), +104 (3H, singlet, $-\text{N}-\text{CH}_3$), +114~+57 (8H, multiplet, $(\text{CH}_3\text{CH}_2)_2\text{N}^+-\text{CH}_2\text{CH}_2-\text{C}-\text{CO}-\text{N}-\text{CH}_2\text{CH}_3$).

2-Amino-2-methyl-4-dimethylaminobutyric Acid (VIIIa)—a) VIIIa from Va: A mixture of Va (1.85 g, 0.01 mole) and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (15.8 g, 0.05 mole) in H_2O (50 ml) was refluxed and stirred for 50 hr. To the reaction mixture was added $(\text{NH}_4)_2\text{CO}_3$ (7.2 g, 0.075 mole), and the BaCO_3 which precipitated was filtered off. The combined filtrate and washings were concentrated to ca. 10 ml and poured through an ion exchange resin (Amberlite IR-120(H^+ form)). The column was washed thoroughly with H_2O and eluted with diluted NH_4OH . The fractions showing positive ninhydrin tests were combined and evaporated to dryness to give crude VIIIa as pale yellow crystals (1.37 g, 86%), mp 253° (decomp.). Three recrystallizations from MeOH-acetone gave pure VIIIa as colorless needles, mp 255° (decomp.). *Anal.* Calcd. for $\text{C}_7\text{H}_{16}\text{O}_2\text{N}_2$: C, 52.47; H, 10.07; N, 17.49. Found: C, 52.55; H, 9.99; N, 17.52. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3420, 2970, 2780, 1610, 1399, 1287, 1186. A paper chromatogram, developed with $\text{BuOH}-\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, 4:1:2 as the solvent system, showed one spot. *Rf* value 0.31.

b) VIIIa from IVa: IVa was treated in a manner similar to Va to afford crude VIIIa (1.5 g, 94%), mp 251—252° (decomp.), which was recrystallized several times from MeOH-acetone to give pure VIIIa as colorless needles, mp 255° (decomp.). *Anal.* Calcd. for $\text{C}_7\text{H}_{16}\text{O}_2\text{N}_2$: C, 52.47; H, 10.07; N, 17.49. Found: C, 52.57; H, 9.90; N, 17.43. The infrared spectrum of this sample was superimposable with that of VIIIa obtained from Va. A paper chromatogram, developed with the same solvent system as in the case of a), showed one spot whose *Rf* value was identical with that of VIIIa from Va.

5-(2-Dimethylaminoethyl)-5-methylhydantoin Na Salt (XI)—A mixture of Va (0.37 g, 0.002 mole) and NaH (50% oil dispersion, 0.1 g, 0.002 mole) in dioxane (20 ml) was stirred at room temperature for 30 min, and refluxed for 2 hr. The reaction mixture was evaporated to dryness *in vacuo* to give hygroscopic crystals (0.42 g), whose infrared spectrum showed characteristic carbonyl bands at 1692, and 1585 cm^{-1} in a solid state.

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Studies on Optically Active Amino Acids. XVI.¹⁾ Studies on α -Alkyl- α -amino Acids. XI.²⁾ Synthesis of *R*- α -Methylphenylalanine from *S*(+)-2-Methyl-3-phenylpropionic Acid by the Direct Conversion of the optically Active C-H Bond into the C-N Bond

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In the previous report,⁴⁾ optically active 2-oxazolidinone (III) was prepared by photochemical decomposition of azidoformate (II), which had been synthesized from carboxylic

1) Part XV: N. Takamura, S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **15**, 1776 (1967).

2) Part X: N. Takamura, S. Terashima and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16**, 2059 (1968).

3) Location: Hongo, Tokyo.

4) S. Terashima and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16**, 1953 (1968).