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Stereochemical Studies. II.[1] Thermal and Photochemical Decompositions of Optically Active Alkyl Azidoformates[2,3]

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The thermal and photochemical decompositions of three types of optically active alkyl azidoformates (III) were attempted, and it was found in both cases, that optically active 2-oxazolidinones (VI) were obtained with nearly complete retention of configuration. The yield of VI was very low (5%) in the thermal decomposition and moderate (25—30%) in the photochemical one. Considering the relationship between stereospecificity and spin mutiplicity of alkoxycarbonyl nitrene (I), a mechanism was proposed suggesting that the singlet state alkoxycarbonyl nitrene (XXX) generated from III, either by heating or by irradiation, had been inserted into the intramolecular optically active C–H bond through the transition state (XXXII).

Moreover, in the course of these studies, the absolute configuration of α-methylphenylglycine(2-amino-2-phenylpropionic acid) was determined using thermal decomposition.

Preliminary experiments using racemic compounds were also reported.

Introduction

Alkoxycarbonyl nitrene (I), generated by the thermal and photochemical decompositions of alkyl azidoformate (II), shows several interesting reactivities for many types of chemical bonds.[5,6] That is, for the aliphatic C–H bonds, I exhibits the so-called insertion reaction to afford N-alkyl carbamates,[7–19] and for the olefinic double bonds 1,2-additions affording

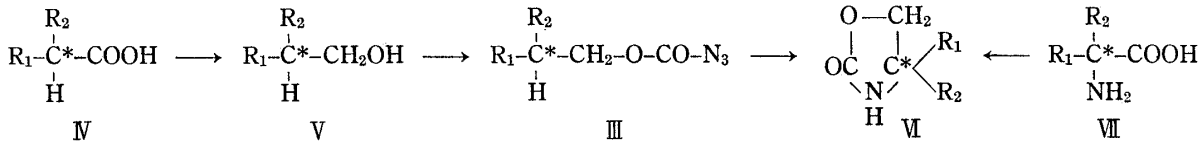
$$\underset{\text{II}}{\text{R-O-CO-N}_3} \xrightarrow{\text{heat or } h\nu} \underset{\text{I}}{\text{R-O-CO-N}}$$

1) Part I: S. Yamada and S. Terashima, *Chem. Pharm. Bull.* (Tokyo), **16**, 1816 (1968).
2) Presented at the 86th and 87th Annual Meetings of Pharmaceutical Society of Japan Sendai, October 1966, and Kyoto, April 1967.
3) Parts of this work have been the subjects of two preliminary reports (ref 48, and 75).
4) Location: *Hongo, Tokyo.*
5) R.A. Abramovitch and B.A. Davis, *Chem. Rev.*, **64**, 149 (1964).
6) *a*) S. Yamada and S. Terashima, *Kagaku*, **21**, 219, 325 (1966); *b*) W. Lwowski, *Angew. Chem.*, **79**, 922 (1967).
7) *a*) W. Lwowski and T.W. Mattingly, Jr., *Tetrahedron Letters*, **1962**, 277; *b*) W. Lwowski and R.L. Johnson, *ibid.*, **1967**, 891.
8) W. Lwowski, and T.J. Maricich, *J. Am. Chem. Soc.*, **86**, 3164 (1964).
9) T.J. Prosser, A.F. Marcantonio, C.A. Genge, and D.S. Breslow, *Tetrahedron Letters*, **1964**, 2483.
10) M.F. Sloan, T.J. Prosser, N.R. Newberg, and D.S. Breslow, *Tetrahedron Letters*, **1964**, 2945.
11) R. Puttner and K. Hafner, *Tetrahedron Letters*, **1964**, 3119.
12) R. Kreher and H. Bockhorn, *Angew. Chem.*, **76**, 681 (1964).
13) G. Smolinsky and B.I. Feuer, *J. Am. Chem. Soc.*, **86**, 3085 (1964).
14) R. Kreher and D. Kuhling, *Angew. Chem.*, **77**, 42 (1965).
15) W. Lwowski and T.W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).
16) W. Lwowski and F.P. Woerner, *J. Am. Chem. Soc.*, **87**, 5491 (1965).
17) H. Nozaki, S. Fujita, H. Tanaka, and R. Noyori, *Tetrahedron*, **23**, 45 (1967).
18) *a*) D.S. Breslow, T.J. Prosser, A.F. Marcantonio, and C.A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967); *b*) D.S. Breslow and E.I. Edwards, *Tetrahedron Letters*, **1967**, 2123.
19) W. Lwowski and J.S. McConaghy, Jr., *J. Am. Chem. Soc.*, **87**, 5490 (1965).

aziridines are observed.[7,15,16,19-22] However, 1,3-dipolar cycloadditions of I to C≡C and C≡N triple bonds give oxazole[23-25] and 1,3,4-oxadiazole[11,26,27] derivatives, respectively. Primary and secondary alcohols are dehydrogenated by I to aldehydes and ketones, respectively,[11,12,28] but for tertiary alcohols the insertion of I to the O–H bond occurs and N-alkoxycarbamates are prepared.[11,12] Aromatic rings disclose many useful reactions involving ring expansion,[7b,29,32] and from the most simple aromatic ring, benzene, I affords N-alkoxycarbonylazepine in a good yield.[29]

As the method for the formation of the optically active C–N bond in a molecule, the authors paid much attention to the insertion reaction of I in the intramolecular C–H bond, since Smolinsky, *et al.*[13] reported that the thermal decomposition of *S*(+)-2-methylbutyl azidoformate(*S*(+)-VIII) in vapour phase led to the formation of optically active (+)-4-ethyl-4-methyl-2-oxazolidinone((+)-IX) in a good yield. In spite of the uncertainty of the absolute configuration and the optical purity of the product, they assumed that this nitrene insertion reaction proceeded with retention of the configuration at the asymmetric carbon, based on the proposed reaction mechanism and the observed optical retention in IX. Moreover, several results,[9,11,12,14,18,27] similar to those of Smolinsky, *et al.*[13] evidently demonstrated that this intramolecular insertion reaction of I was very common.

The results cited above prompted us to investigate the thermal and photochemical decompositions of optically active alkyl azidoformate (III) prepared from carboxylic acid (IV) or the alcohol (V), whose absolute configuration and optical purity is already known. We also elucidated the retention percent of optical activity for 2-oxazolidinone (VI) obtained as the insertion product and the steric course of the insertion reaction, by comparison with the authentic VI, synthesized independently from the α-alkyl-α-amino acid (VII), whose absolute configuration and optical purity is already known.



Results

a) Thermal Decomposition of Optically Active Alkyl Az oformates

First, in order to establish the absolute configuration and the optical purity of (+)-IX, which Smolinsky, *et al.*[13] had obtained from the thermal decomposition of *S*(+)-VIII in the vapour phase, the independent synthesis of optically active (+)-IX from *R*(−)-isovaline

20) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, **1964**, 3953.
21) I. Brown and O.E. Edwards, *Canad. J. Chem.*, **43**, 1266 (1965).
22) *a*) J.S. McConaghy, Jr., and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967); *b*) *Idem*, *ibid.*, **89**, 4450 (1967).
23) R. Huisgen and H. Blaschke, *Tetrahedron Letters*, **1964**, 1409.
24) R. Huisgen and H. Blaschke, *Chem. Ber.*, **98**, 2985 (1965).
25) J. Meinwald and D.H. Aue, *J. Am. Chem. Soc.*, **88**, 2849 (1966).
26) W. Lwowski, A. Hartenstein, C. deVita, and R.L. Smick, *Tetrahedron Letters*, **1964**, 2497.
27) R. Huisgen and H. Blaschke, *Ann.*, **686**, 145 (1965).
28) T.J. Prosser, A.F. Marcantonio, and D.S. Breslow, *Tetrahedron Letters*, **1964**, 2479.
29) K. Hafner and C. König, *Angew. Chem.*, **75** 89 (1963).
30) R.J. Cotter and W.F. Beach, *J. Org. Chem.*, **29**, 751 (1964).
31) K. Hafner and W. Kaiser, *Tetrahedron Letters*, **1964**, 2185.
32) K. Hafner, D. Zinzer, and K.L. Moritz, *Tetrahedron Letters*, **1964**, 1733.

($R(-)$-X), whose absolute configuration[33] and optical purity is already determined by us,[34,35] was undertaken. The chemical scheme employed is shown in Chart 1. Preliminary experiments on racemic compounds were examined in order to find out optimal working conditions.

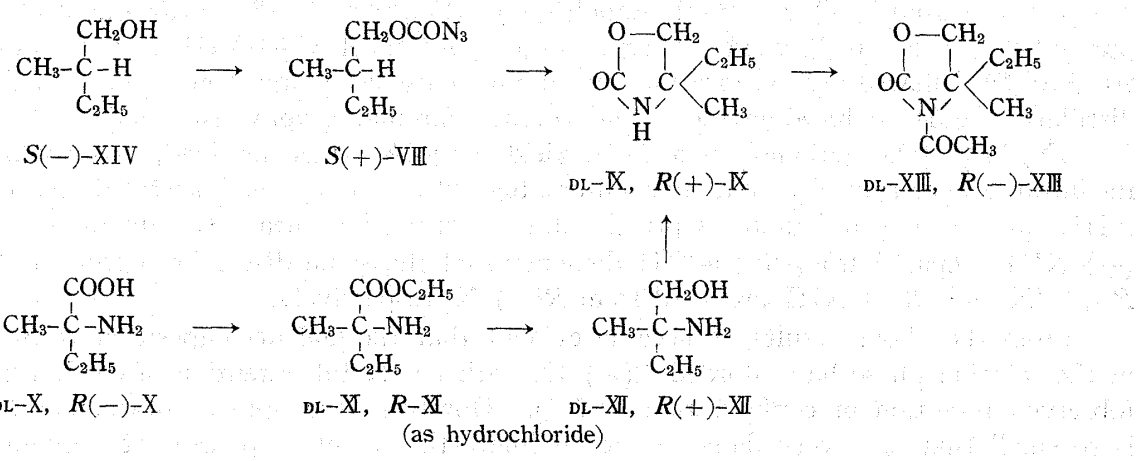


Chart 1

Reflux of DL-isovaline(DL-X)[34,36] with thionyl chloride in ethanol gave DL-isovaline ethyl ester (DL-XI)[37] in a 70% yield, which was reduced with sodium borohydride in aqueous ethanol[38] to afford DL-2-amino-2-methylbutanol(DL-XII)[39] in a 35% yield. Diethyl carbonate solution containing DL-XII, thus obtained, and a catalytic amount of sodium methoxide were refluxed for 4 hr[40] to give DL-4-ethyl-4-methyl-2-oxazolidinone(DL-IX) in a 77% yield, whose nuclear magnetic resonance spectrum was almost identical with that reported by Smolinsky, *et al.*[13] DL-IX was converted to DL-3-acetyl-4-ethyl-4-methyl-2-oxazolidinone(DL-XIII) in a 95% yield by reflux in acetic anhydride with sodium acetate.[40]

Next, esterification of $R(-)$-isovaline($R(-)$-X), $[\alpha]_D^{12}$ $-5.4°$ (H_2O), optical purity 45%,[34,35] and $S(+)$-isovaline($S(+)$-X), $[\alpha]_D^{16}$ $+6.9°$ (H_2O), optical purity 58%,[34,35] obtained from the resolution of DL-X by the method of Akabori, *et al.*,[41] yielded R-XI and S-XI-hydrochlorides, respectively, which in this case, without isolation, were treated with sodium borohydride,[38] in a manner similar to the case of DL-XI, to afford $R(+)$-2-amino-2-methylbutanol ($R(+)$-XII),[13] $[\alpha]_D^{15}$ $+1.2°$ (ethanol) and $S(-)$-XII, $[\alpha]_D^{13}$ $-2.0°$ (ethanol) in a 11% and 18% yield, respectively. $R(+)$-XII was treated the same as DL-XII to give $R(+)$-IX, $[\alpha]_D^{12}$ $+1.0°$ (ethanol) in a 67% yield, which was identified from its infrared spectrum and by its conversion to $R(-)$-3-acetyl-4-ethyl-4-methyl-2-oxazolidinone($R(-)$-XIII), $[\alpha]_D^{12}$ $-6.9°$ (ethanol).

From the results obtained above, the thermal decomposition of $S(+)$-VIII in the vapour phase as performed by Smolinsky, *et al.*[13] appeared to proceed with the retention of configuration. However, contrary to our expectation, it became evident that the retention percent of

33) *a*) S. Yamada and K. Achiwa, *Chem. Pharm. Bull.* (Tokyo), **12**, 1525 (1964); *b*) K. Achiwa and S. Yamada, *ibid.*, **14**, 537 (1966).
34) S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **13**, 1399 (1965).
35) The maximum optical rotation, $[\alpha]_D^{21}$ $-11.9°$ (H_2O), among those reported in the literature (see ref. 34) is assumed to be 100% optically pure, and some differences in the temperature at which the measurements of optical rotation were carried out was neglected.
36) R.A. Levene and R.E. Steiger, *J. Biol. Chem.*, **76**, 299 (1928).
37) *a*) L.Li, K-H, Lin, Y-T, Huang, and S-A, Kang, *J. Chinese Chem, Soc.*, **9**, 1 (1942); *b*) M.D. Slimmer, *Chem. Ber.*, **35**, 400 (1902).
38) H. Seki, K. Koga, H. Matsuo, T. Oki, I. Matsuo, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **13**, 995 (1965).
39) H.B. Hass and B.M. Vanderbilt, U.S. patent 2139120 [*C.A.*, **33**, 2149^7 (1939)].
40) A.H. Homeyer, U.S. patent 2399118 [*C.A.*, **40**, 4084^5 (1946)].
41) S. Akabori, T. Ikenaka, and K. Matsuki, *Nippon Kagaku Zasshi*, **73**, 112 (1952).

optical activity of $R(+)$–IX was low,[42] so that a reexamination of the thermal decomposition of $S(+)$–VIII in the solution phase was attempted by us.

According to the method of Smolinsky, *et al.*,[13] $S(+)$–VIII, α_D^{11} +2.296° (l=0.5, neat) was prepared from $S(-)$–2–methylbutanol($S(-)$–XIV),[43,44] α_D^{10} −2.092° (l=0.5, neat), optical purity 84%,[45] in a 64% yield. Thermal decomposition of $S(+)$–VIII in diphenyl ether at 200±10°,[46] followed by purification by column chromatography on alumina, subsequent distillation under reduced pressure, and column chromatography using silica gel, afforded (+)–IX, $[\alpha]_D^8$ +2.0° (ethanol) in a 7.0% yield. (+)–IX, thus obtained, was confirmed by its infrared spectrum, by thin-layer chromatography, and by its 3–acetyl derivative ((−)–XIII), $[\alpha]_D^9$ −10.8° (ethanol). Optical rotatory dispersion measurements of (+)–IX and (−)–XIII prepared from $S(+)$–VIII demonstrated the same dispersion curves as those of $R(+)$–IX and $R(-)$–XIII prepared from $R(-)$–X, respectively.

From the above results, it became evident that thermal decomposition of $S(+)$–VIII in the solution phase had afforded $R(+)$–IX with nearly full retention of configuration[47,48] (observed retention of configuration, 107%). However, the optical rotation of $R(+)$–IX is so small that it is very dangerous to estimate the retention percent of configuration in detail from the optical purity of $R(+)$–IX. Furthermore, in order to examine the retention percent of configuration of this thermal decomposition in solution phase in detail, the thermal decomposition of 2–methyl–3–phenylpropyl azidoformate (XV) was undertaken.

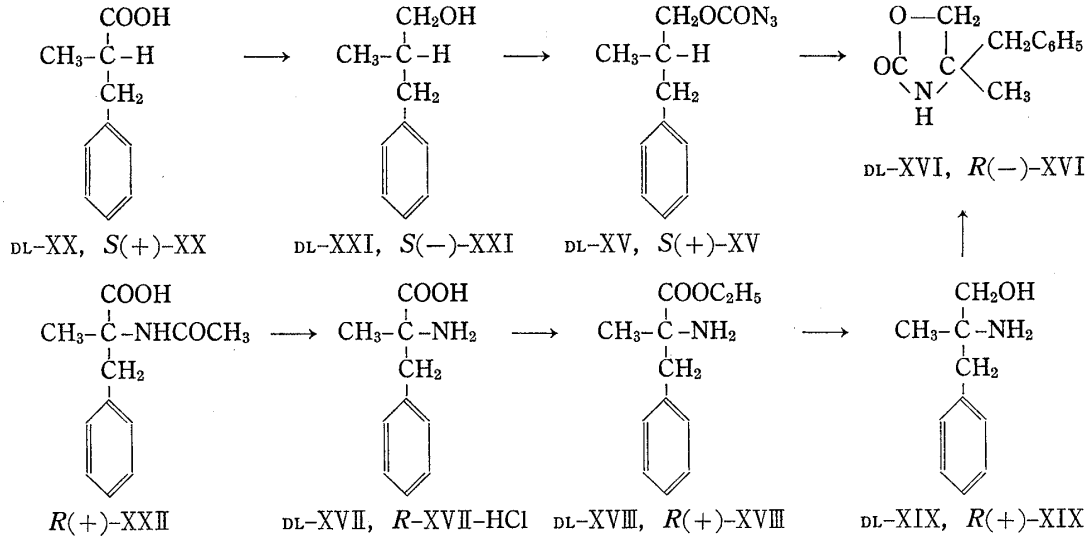


Chart 2

42) Since $R(+)$–IX showing $[\alpha]_D^{12}$ +1.0° (ethanol) was assumed to be 45% optically pure, the optical purity of (+)–IX, $[\alpha]_D^{25}$ +0.354° (ethanol), obtained by Smolinsky, *et al.*[13] could be calculated at an optical purity of 16%. From the optical purity of (+)–IX, and that of $S(+)$–VIII, it became obvious that thermal decomposition of $S(+)$–VIII in the vapour phase had proceeded with 21% retention of configuration.

43) The absolute configuration of (−)–XIV has already been established to be S–series by chemical correlation with L(+)–lactic acid (see J. Kenyon, H. Phillips, and V. Pittman, *J. Chem. Soc.*, **1935**, 1072; P.A. Levene, *et al.*, *J. Biol. Chem.*, **65**, 49 (1925); *ibid.*, **67**, 329 (1926); *ibid.*, **69**, 165 (1926); *ibid.*, **71**, 465 (1927); W. Marckward, *Chem. Ber.*, **37**, 1038 (1904)).

44) W. Marckwald and A. McKenzie, *Chem. Ber.*, **34**, 490 (1901).

45) $S(-)$–XIV showing $[\alpha]_D^{20}$ −5.90° (neat), d_D^{20} 0.816 (see ref. 44) was assumed to be 100% optically pure and, in this case, the difference of temperature at which the measurements of optical rotation were performed was corrected by using another sample of $S(-)$–XIV.

46) G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 2489 (1961).

47) Since $R(+)$–IX showing $[\alpha]_D^{12}$ +1.0° (ethanol) was 45% optically pure, the optical purity of (+)–IX, $[\alpha]_D^8$ +2.0° (ethanol) became 90%.

48) S. Yamada, S. Terashima, and K. Achiwa, *Chem. Pharm. Bull.* (Tokyo), **13**, 751 (1965).

Here, also, preliminary examinations of the reaction conditions were performed with racemic compounds before the optically active compounds were examined.

As shown in Chart 2, DL-4-benzyl-4-methyl-2-oxazolidinone(DL-XVI) was prepared from DL-α-methylphenylalanine (DL-XVII)[49] in a manner similar to the preparation of DL-IX, by way of DL-α-methylphenylalanine ethyl ester (DL-XVIII),[50] in a 74% yield from DL-XVII, and DL-2-amino-2-methyl-3-phenylpropanol (DL-XIX) in a 71% yield from DL-XVIII. The yield of DL-XVI from DL-XIX was 79%. The DL-XVI thus obtained was confirmed by elemental analysis, and by its infrared and nuclear magnetic resonance spectra.

Reduction of DL-2-methyl-3-phenylpropionic acid (DL-XX)[51] with lithium aluminum hydride in ether[52] gave DL-2-methyl-3-phenylpropanol (DL-XXI)[53] in a 78% yield. The same treatment of DL-XXI as in the case of S(−)-XIV afforded DL-XV in a 98% yield, which, without purification, was decomposed thermally in diphenyl ether at 200±10°[46,48] followed by the same purification methods as those described in the decomposition of S(+)-VIII, to give DL-XVI in a 5.0% yield. DL-XVI, thus prepared, was identified with the authentic DL-XVI obtained previously by its mixed melting point and spectral data.

The same procedures as those cited for the racemic compounds were repeated again on the optically active compounds. Esterification of R-α-methylphenylalanine hydrochloride (R-XVII-HCl) prepared from (+)-N-acetyl-R-α-methylphenylalanine(R(+)-XXII), $[\alpha]_D^{25}$ +75.0° (methanol), optical purity 100%,[49] afforded R(+)-α-methylphenylalanine ethyl ester (R(+)-XVIII), α_D^{23} +1.182° (l=0.1, neat), in an 81% yield. Reduction of R(+)-XVIII similar to that of DL-XVIII[38] gave R(+)-2-amino-2-methyl-3-phenylpropanol(R(+)-XIX), $[\alpha]_D^{21}$ +4.8° (ethanol), which was converted to R(−)-4-benzyl-4-methyl-2-oxazolidinone (R(−)-XVI), $[\alpha]_D^{25}$ −28.8° (ethanol), in a 72% yield. R(−)-XVI thus prepared was confirmed by elemental analysis and its spectral data.

On the other hand, S(+)-XX, α_D^{21} +1.939° (l=0.1, neat), optical purity 74%,[51,54] prepared from the resolution of DL-XX with quinine,[51] was reduced, in the same way as DL-XX,[52] to afford S(−)-2-methyl-3-phenylpropanol(S(−)-XXI), α_D^{23} −0.964° (l=0.1, neat), in a 66% yield. S(+)-2-methyl-3-phenylpropyl azidoformate (S(+)-XV), α_D^{21} +1.644° (l=0.1, neat), obtained from S(−)-XXI was decomposed in the same way as DL-XV to give (−)-XVI, $[\alpha]_D^{24}$ −20.7° (ethanol), in a 6.2% yield.[55] This was identified with the authentic R(−)-XVI from its infrared spectrum, its mixed melting point measurement, optical rotatory dispersion curve, and by gas chromatographic analysis. Comparing the optical purity of R(−)-XVI, prepared from R(+)-XXII, with that of R(−)-XVI synthesized from S(+)-XX, it appeared evident that R(−)-XVI was obtained from S(+)-XV with 97% retention of configuration in the thermal decomposition of its solution phase.

From these two examples, it is clearly concluded that intramolecular insertion reaction of I, generated thermally from III, into the optically active C–H bond proceeded with nearly full retention of configuration.

The results obtained here suggest that this intramolecular insertion reaction of I can not be used for the preparation of optically active VI from the synthetic point of view because of the low yield of VI, but it may be applicable to one of the methods for the determination

49) S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **14**, 1139 (1966).
50) T.N. Ghosh and B. Bhattacharya, *J. Indian Chem. Soc.*, **34**, 863 (1957).
51) S. Terashima and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16**, 1816 (1968).
52) *a*) K.B. Wiberg and T.W. Hutton, *J. Am. Chem. Soc.*, **78**, 1640 (1956); *b*) E.L. Eliel and J.P. Freeman, *ibid.*, **74**, 928 (1952).
53) *a*) L. Li, W.H. Elliott, *J. Am. Chem. Soc.*, **74**, 4089 (1952); *b*) C. Weizmann, E. Bergmann, and L. Halshelburg, *Chem. Ind.*, **1937**, 587; *c*) J.v. Brown, A. Grabowski, and G. Kirshbaum, *Chem. Ber.*, **46**, 1266 (1913).
54) See ref. 51 and the foot note 27 therein.
55) Based on the assumption that R(−)-XVI, showing $[\alpha]_D^{25}$ −28.8° (ethanol), was optically pure, the optical purity of (−)-XVI obtained from S(+)-XV was calculated to be 72%.

of absolute configuration of a carboxylic acid (IV) which has an optically active tertiary C–H bond at the α-position, or of an α-alkyl-α-amino acid (VII) with regard to the reaction mechanism, if either one of the absolute configurations can be established.

On the absolute configuration of α-methylphenylglycine (2-amino-2-phenylpropionic acid) (XXIII), which is one of the important α-alkyl-α-amino acids used frequently for studies on the reaction mechanism,[56–61] two opposite suggestions have been proposed. Cram, *et al.*[60] deduced the absolute configuration of (+)-XXIII to be *S*-series from Freudenberg's displacement rule and their studies on carbanion chemistry.

On the other hand, Maeda[59] assumed that (+)-XXIII was either *R*- or D-series without any convincing evidence. The discrepancy in the assignments cited above prompted us to examine the correlation of the absolute configuration of XXIII with that of hydratropic acid (2-phenylpropionic acid) (XXIV), whose absolute configuration has already been established,[62,63] using thermal decomposition of the azidoformate prepared from XXIV.

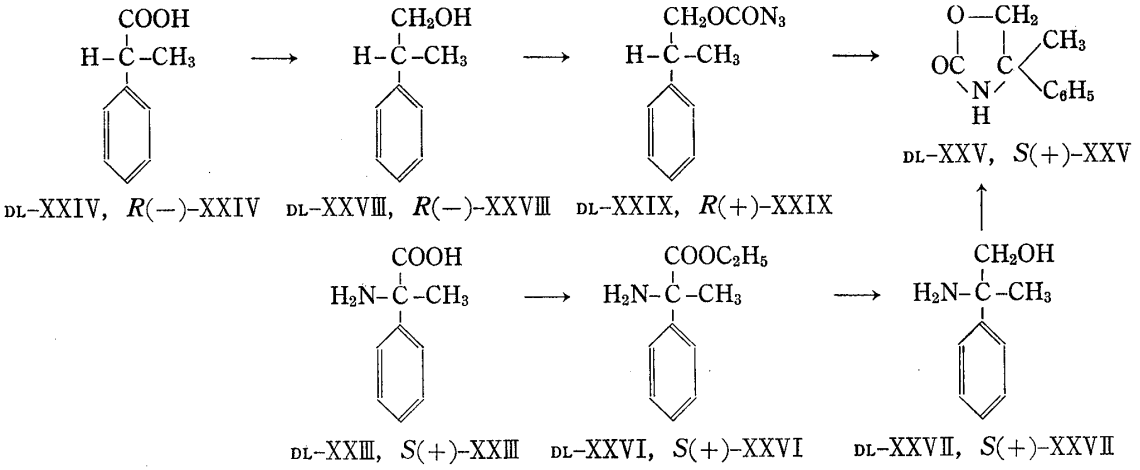


Chart 3

The chemical scheme we employed is illustrated in Chart 3. In this case also, before the optically active compounds were attempted, preliminary examinations using racemic compounds were performed.

As same as the cases of DL-X and DL-XVII, DL-XXIII[64] was converted to DL-4-methyl-4-phenyl-2-oxazolidinone (DL-XXV)[40,65] by way of DL-α-methylphenylglycine ethyl ester (DL-XXVI)[66] and DL-2-amino-2-phenylpropanol (DL-XXVII).[38,65] The DL-XXV obtained was confirmed by its spectral data, and its melting point which was identical with that reported.[65]

56) A. McKenzie and G.W. Clough, *J. Chem. Soc.*, **101**, 390 (1912).
57) A. McKenzie and J. Myles, *Chem. Ber.*, **65**, 209 (1932).
58) W.A. Bonner and J.A. Zderic, *J. Am. Chem. Soc.*, **78**, 3218 (1956).
59) G. Maeda, *Nippon Kagaku Zasshi*, **77**, 1011 (1956).
60) D.J. Cram, L.K. Gaston, and H. Jäger, *J. Am. Chem. Soc.*, **83**, 2183 (1961).
61) S. Mitsui and E. Sato, *Nippon Kagaku Zasshi*, **86**, 416 (1965).
62) The absolute configuration of XXIV has been clearly established by chemical correlations with L(+)-alanine and L(+)-lactic acid (see ref. 63).
63) *a*) W.A. Bonner and J.A. Zderic, *J. Am. Chem. Soc.*, **81**, 3336 (1959) and the ref. 15—22 therein; *b*) F.A.A. Elhafez and D.J. Cram, *ibid.*, **74**, 5846 (1952) and the ref. 9 therein; *c*) W.A. Bonner, J.A. Zderic, and G.A. Casalette, *ibid.*, **74**, 5086 (1952) and the ref. 6—11 therein.
64) *Org. Syn.*, Coll. Vol. III, p. 88.
65) M.S. Newman and W.M. Edwards, *J. Am. Chem. Soc.*, **76**, 1840 (1954).
66) H. Adkins and H.R. Billica, *J. Am. Chem. Soc.*, **70**, 3121 (1948).

Reduction of DL–XXIV[67] similar to that of DL–XX afforded DL–2–phenylpropanol (DL–XXVIII),[52b,68] which was converted to DL–2–phenylpropyl azidoformate (DL–XXIX) by the same treatment as in the case of *S*(−)–XIV.[13] Thermal decomposition of DL–XXIX in diphenyl ether at 200±10°[13,46] was followed by the same purification methods, as used for the decomposition of *S*(+)–VIII, gave DL–XXV in a 3.7% yield, which was identified with the authentic DL–XXV prepared above.

Crude (+)–α–methylphenylglycine((+)–XXIII) (optical purity 82%)[69] obtained from the resolution of DL–XXIII[56] was treated in the same way as DL–XXIII to afford (+)–α–methylpheylglycine ethyl ester ((+)–XXVI),[57,58,60] α_D^{16} +0.993° (*l*=0.1, neat), optical purity 89%,[70] which was converted to (+)–4–methyl–4–phenyl–2–oxazolidinone((+)–XXV),[40] $[\alpha]_D^{27}$ +101° (ethanol), through (+)–2–amino–2–phenylpropanol((+)–XXVII),[38] $[\alpha]_D^{23}$ +14.3° (ethanol). (+)–XXV was identified by elemental analysis and from spectral data.

On the other hand, reduction[52b] of *R*(−)–hydratropic acid (*R*(−)–XXIV), $[\alpha]_D^{24}$ −33.7° (ethanol), optical purity 42%,[71,72] which was prepared from the resolution of DL–XXIV,[72] afforded *R*(+)–2–phenylpropanol(*R*(+)–XXVIII),[52b,73] α_D^{24} +0.717° (*l*=0.1, neat), optical purity 40%.[74] The *R*(+)–XXVIII thus obtained was led to *R*(+)–2–phenylpropyl azidoformate (*R*(+)–XXIX), α_D^{23} +0.222° (*l*=0.1, neat) in the same manner as DL–XXVIII, and without purification, was decomposed thermally in diphenyl ether at 200±10°[13,46] to afford (+)–XXV, $[\alpha]_D^{25}$ +43.9° (ethanol), in a 4.0% yield. The (+)–XXV obtained was identified from its infrared spectrum and by thin-layer chromatography. Recrystallizations of (+)–XXV showing $[\alpha]_D^{25}$ +43.9° (ethanol) gave (+)–XXV with a low optical purity, $[\alpha]_D^{17}$ +9.3° (ethanol).

From the results obtained above, it was concluded that the absolute configuration of (+)–XXIII should be given as the *S*–configuration on the assumption that thermal decomposition of *S*(+)–XXIX had proceeded with the retention of configuration the same as in the case of *S*(+)–VIII and *S*(+)–XV. This conclusion was in agreement with Cram's proposal.[60,75]

After completion of the determination for the absolute configuration of (+)–XXIII, as described above, another determination of the absolute configuration using the chemical correlation method was accomplished,[76] and confirmed our first determination.[75]

Consequently, it became evident that thermal decomposition of *R*(+)–XXIX in the solution phase afforded *S*(+)–XXV with 93% or 98% retention of configuration based on the optical purity of *R*(+)–XXIX.[77]

The yield of VI and the percent of retention for configuration observed in the thermal decomposition of three types of optically active V, in diphenyl ether, are summarized in Table I.

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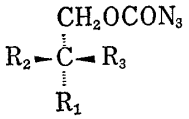
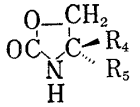
67) *a*) *Org. Syn.*, Coll. Vol. III. p. 727, 733; *b*) C.L. Arcus and J. Kenyon, *J. Chem. Soc.*, **1939**, 916.
68) *a*) P. Rampart and P. Amagat, *Ann. Chim.*, **8**, 263 (1927); *b*) L.F. Hatch and T.L. Patton, *J. Am. Chem. Soc.*, **76**, 2705 (1954); *c*) C. Golumbic and D.L. Cottle, *J. Am. Chem. Soc.*, **61**, 1000 (1939).
69) Maximum optical rotation, $[\alpha]_D^{19}$ −90.3° (*c*=2.74, 1N HCl) (see ref. 56). This was assumed to be optically pure.
70) (+)–XXVI showing α_D^{24} +12.14° (*l*=1, neat) prepared from (+)–XXIII, $[\alpha]_D^{20}$ +70 3° (H_2O) by Cram, *et al.* (see ref. 60) was assumed to be 100% optically pure, and the temperature difference in the measurements of optical rotation was corrected using (−)–XXVI (see experimental).
71) Maximum optical rotation, $[\alpha]_D^{20}$ +81.1° (*c*=3.108, ethanol), among those measured in ethanol, was assumed to be 100% optically pure (see ref. 72).
72) H.S. Raper, *J. Chem. Soc.*, **123**, 2558 (1925).
73) J.B. Cohen, J. Marshall, and H.E. Woodman, *J. Chem. Soc.*, **107**, 899 (1915).
74) Eliel, *et al.* reported that (+)–XXVIII showing $\alpha_D^{25.5}$ +6.37±0.02° (*l*=2, neat) was 17.7% optically pure (see ref. 52*b*).
75) S. Yamada, S. Terashima, and K. Achiwa, *Chem. Pharm. Bull.* (Tokyo), **14**, 800 (1966).
76) H. Mizuno, S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **15**, 1749 (1967).
77) When the optical purity of *R*(+)–XXIX was assumed to be 42%, the percent of retention for *S*(+)–XXV became 93%. On the other hand, the percent of retention for *S*(+)–XXV was calculated to be 98% when the optical purity of *R*(+)–XXIX was assumed to be 40% (see experimental).

Table I. The Thermal Decomposition of Alkyl Azidoformates in Diphenyl Ether



Alkyl azidoformates



2-Oxazolidinones

R_1	R_2	R_3	R_4	R_5	Yield (%)	Observed retention of configuration (%)
C_2H_5	CH_3	H	C_2H_5	CH_3	7.0	107
$C_6H_5CH_2$	CH_3	H	$C_6H_5CH_2$	CH_3	6.2	97
C_6H_5	H	CH_3	CH_3	C_6H_5	4.0	93 or 98

Table II. The Photochemical Decomposition of Alkyl Azidoformates

Run	Starting material	Optical purity (%)	Reaction condition	Solvent	Irradiation time (hr)
1	DL-XV		H[a]	CH_2Cl_2	2
2	DL-XV		H	CCl_4	2
3	DL-XV		L[c]	CH_2Cl_2	8
4	S(+)-XV	84	H	CH_2Cl_2	2
5	S(+)-XV	84	H	CCl_4	2
6	S(+)-XV	84	L	CH_2Cl_2	8
7	S(+)-VIII	86	L	CH_2Cl_2	8

Run	2-Oxazolidinones		Yield (%)	$[\alpha]_D$ (C_2H_5OH)	Observed retention of configuration (%)	Azidoformate recovered		
	R_1	R_2				Compd.	Yield (%)	α_D (l=0.1, neat)
1	$C_6H_5CH_2$	CH_3	12[b]					
2	$C_6H_5CH_2$	CH_3	6[b]					
3	$C_6H_5CH_2$	CH_3	25					
4	$C_6H_5CH_2$	CH_3	14	$[\alpha]_D^{28}$ −24.8°	105[d]	S(+)-XV	49	α_D^{24} +2.335°
5	$C_6H_5CH_2$	CH_3	11	$[\alpha]_D^{25}$ −24.9°	104[e]	S(+)-XV	47	α_D^{28} +2.230°
6	$C_6H_5CH_2$	CH_3	27	$[\alpha]_D^{30}$ −24.1°	101[d]			
7	C_2H_5	CH_3	30	$[\alpha]_D^{15}$ + 2.0°	105[f]			

a) high pressure mercury lamp (400 w)
b) Recovery of the unreacted DL-XV was not attempted.
c) low pressure mercury lamp (30 w)
d) R(−)-XVI showing $[\alpha]_D^{30}$ −28.3° (C_2H_5OH) was assumed to be optically pure.
e) R(−)-XVI showing $[\alpha]_D^{25}$ −28.8° (C_2H_5OH) was assumed to be optically pure.
f) R(+)-IX showing $[\alpha]_D^{12}$ +1.0° (C_2H_5OH) was assumed to be 45% optically pure.

b) Photochemical Decomposition of Optically Active Alkyl Azidoformates

The photochemical decomposition of the optically active alkyl azidoformates, S(+)-VIII and S(+)-XV, prepared in the same manner as a), was studied and the results obtained are summarized in Table II. The photochemical decomposition was carried on in a nitrogen atmosphere with ice cooling, using either a high pressure mercury lamp (400 W) or the low pressure mercury one (30 W) manufactured by Rikosha, Ltd.

When a high pressure mercury lamp was used as the light source, the photochemical decomposition was stopped after 2 hr of irradiation because of the difficulty in keeping the temperature of the reaction mixture below 25°. In this case nearly 50% of the starting material was recovered. However, when the low pressure mercury lamp was chosen as the light source, the irradiation was continued for 8 hr. Thin-layer chromatography of the residual oil, obtained by evaporation of the reaction mixture after irradiation ceased, clearly disclosed an almost complete absence of starting material. The yield of VI was not less than 15% when the high pressure mercury lamp was used, and not less than 30% when the decomposition was performed using the low pressure mercury lamp. (+)-4-Ethyl-4-methyl-2-oxazolidinone ((+)-IX) and (−)-4-benzyl-4-methyl-2-oxazolidinone((−)-XVI) obtained from *S*(+)-VIII and *S*(+)-XV by photochemical decomposition, respectively, were identified with authentic samples whose absolute configuration and optical purity are already established. From Table II, it be seen that, similar to thermal decomposition in the solution phase, photochemical decomposition of optically active III in its solution phase can also afford VI with the retention of configuration, and the extent of the percent of retention in this reaction was nearly 100%. Moreover, since this yield of optically active VI was higher than that by thermal decomposition, it may be possible to apply this photochemical decomposition of III in the solution phase for synthetic purposes

Discussion

That the thermal and photochemical decompositions of optically active III gave VI with almost complete retention of configuration can be reasonably explained from the results which have been reported in nitrene chemistry literature.[5,6,15,16,19,22,78] As shown in Chart 4, in thermal decomposition the vibrational excitation of III from heating causes the elimination of a nitrogen molecule, from the exicted III, to afford the singlet state alkoxycarbonyl nitrene (XXX). Before converting to the ground state triplet state alkoxycarbonyl nitrene (XXXI) under the intersystem crossing, this species can attack the intramolecular optically active C–H bond to give an optically active insertion prodouct (VI) through the insertion transition state such as XXXII. The transition state, XXXII, seemsto be of the same nature as that

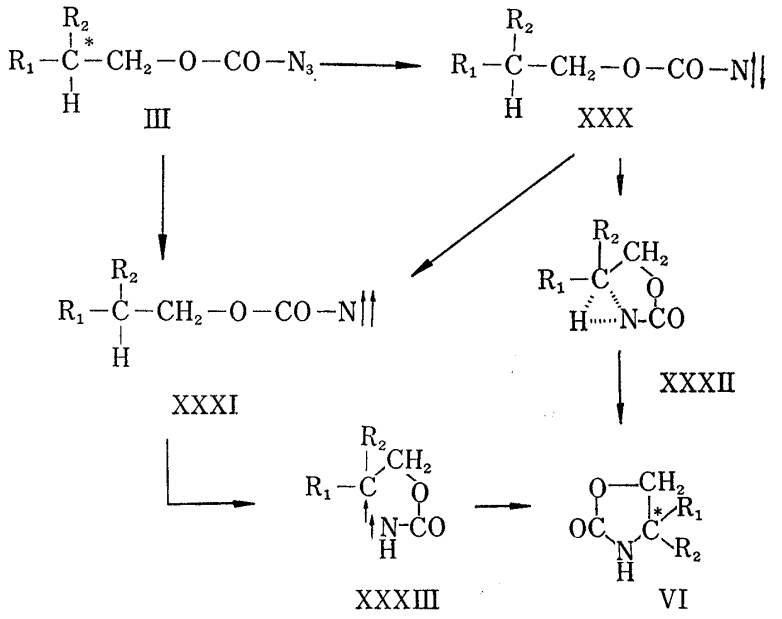


Chart 4

78) P Scheiner, *J. Am. Chem. Soc.*, **88**, 4759 (1966).

used by Smolinsky, *et al.*[13] to explain the retention of optical activity observed in the preparation of *R*(+)-IX from *S*(+)-VIII. The preparation of VI from XXXI should pass through a biradical transition state such as XXXIII. In such a transition state, racemization by the carbon–carbon bond rotation must be inevitable since the rate of bond rotation is faster than that of spin inversion followed by carbon–nitrogen bond formation.[19,22,78] The nearly complete retention of configuration observed for VI clearly demonstrates that the mechanism by way of XXXI and XXXIII would not participate in the formation of VI.

In photochemical decomposition in the solution phase, it seems possible that not only XXX but also XXXI can be generated from electronically excited III. Moreover, XXX can convert to the more stable XXXI as in the case of thermal decomposition. However, the almost complete retention of configuration, also observed in photochemical decomposition, discloses clearly that VI has been prepared exclusively from XXX through the transition state XXXII.

The reason why the insertion reaction of XXX has occurred on the intramolecular optically active C–H bond, is that the optically active C–H bond is the most reactive for XXX due to the electronic effect.[8,10,18,79] It also occupies the most favorable position for intramolecular cyclization from a stereochemical point of view.[5]

Lwowski[6b,16] and Nozaki[17] reported, independently, that the intermolecular insertion reaction of alkoxycarbonyl nitrene (I) proceeded mainly through the singlet state. Their results seem to be compatible with those obtained by us.

The reason why XXXI has given no intramolecular insertion product seems to be that the hydrogen abstraction and the radical dimerization reaction typical of the triplet state nitrenes[17] are more favorable reaction courses for XXXI than the intramolecular insertion reaction. However, we feel this assumption to be less convincing since no examination for the isolation of products expected to occur from XXXI exclusively, has been attempted.

The lower yield of VI by thermal decomposition than by photochemical decomposition may be accounted for by the fact that diphenyl ether being more reactive for nitrenes than methylene dichloride[11,17,19] has been used as the reaction solvent, and that the decomposition has been carried on in a relatively high concentration of III moreover, for a short period of time.

Experimental[80]

DL-Isovaline (DL-X) and Its Resolution——DL–X was prepared by the method reported by Levene, *et al.*[36] and resolved according to the method of Akabori, *et al.*[41,81] *S*(+)-X-H_2O,[33] $[\alpha]_D^{16}$ +6.9° (*c*=4.23, H_2O), optical purity 58%,[34,35] and *R*(−)-X-H_2O,[33] $[\alpha]_D^{12}$ −5.4° (*c*=2.03, H_2O), optical purity 45%[34,35] were obtained as fine needles.

DL-Isovaline Ethyl Ester (DL-XI)——To a suspension of anhyd. DL–X[82] (18.4 g, 0.157 mole) in EtOH (200 ml) was added $SOCl_2$ (93.4 g, 0.785 mole) dropwise, over a 50 min period with stirring and ice cooling. The whole was refluxed for 6 hr with stirring, and then evaporated to dryness. The residue was dissolved in H_2O (50 ml), and $NaHCO_3$ (15 g) was added to the aqueous layer, which was extracted with ether (50 ml ×2). An additional amount of $NaHCO_3$ (5 g) was added to the aqueous layer and extraction with ether (50 ml×1) was repeated. Addition of NaOH pellets (2 g and then 4 g) to the aqueous layer followed by extraction with ether (50 ml×1 and then 50 ml×2) was again repeated. All the ether layers were combined and dried with anhyd. K_2CO_3. Filtration and evaporation gave a pale yellow oil (19.8 g), which was sub-

79) W. Lwowski and T.J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).

80) All the melting points and boiling points were uncorrected. IR spectra measurements were performed with a Spectrometer, Model DS-402 and IR-S, Japan Spectroscopic Co. Ltd. NMR spectra were determined with a Spectrometer Model 3H-60, Japan Electron Optics Lab. Optical activities were measured with a Yanagimoto Photo Direct Reading Polarimeter, Model OR-20. ORD curve measurements were carired out with a Spectrometer Model ORD/UV-5, Japan Spectroscopic Co. Ltd. Gas chromatographic analyses were performed using a Yanagimoto Gas Chromatograph, Model GCG-3D.

81) S. Terashima, K. Achiwa, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **14**, 572 (1966).

82) DL–X–H_2O was dried for 5 hr at 125—135° under reduced pressure (6 mmHg).

mitted to fractional distillation to afford DL–XI as a colorless oil (15.9 g, 70%), bp 67° (20—21.5 mmHg). Further distillation of the DL–XI obtained above, gave a pure sample as a colorless oil, bp 67—68° (20 mmHg) (lit.,[37a] bp 65—66° (20 mmHg); lit.,[37b] bp 65—66° (20 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3385, 3355, 1730, 1600, 1219, 1140.

DL-2-Amino-2-methylbutanol (DL-XII)——A mixture of DL–XI (18.5 g, 0.128 mole) and $NaBH_4$ (24.1 g, 0.637 mole) in 75% aq. EtOH (150 ml) was refluxed for 8 hr with stirring.[38] After standing at room temperature overnight, the precipitates were filtered off and the filtrate was concentrated *in vacuo* to *ca.* 50 ml. To the residual solution was added H_2O (50 ml) and ether (50 ml), and the aqueous layer was saturated with NaCl. After the addition of NaOH (1 g) to the aqueous layer, extraction on the upper ether layer, was performed. The aqueous layer was further extracted with ether (50 ml × 3). The combined ether layers were washed with satd. NaCl (50 ml × 1), and dried with anhyd. K_2CO_3. Filtration and evaporation *in vacuo* afforded a yellow oil (8.7 g), to which was applied fractional distillation yielding DL–XII as a colorless oil (4.3 g, 35%). This oil distilled out up to bp 77° (10 mmHg) (lit.,[39] bp 180°; lit.,[13] bp 80—82° (12 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3340, 3270, 1591, 1057.

Acid oxalate was obtained as white crystals, mp 154.5—155° (recrystallized from aq. EtOH). *Anal.* Calcd. for $C_7H_{15}O_5N$: C, 43.51; H, 7.83; N, 7.25. Found: C, 43.63; H, 7.66; N, 7.25. IR ν_{max}^{KBr} cm^{-1}: 3400, 1721, 1703, 1617, 1108, 1080, 1050.

***S*(−)- and *R*(+)-2-Amino-2-methylbutanol (*S*(−)- and *R*(+)-XII)**——Anhyd. *S*(+)–X ($[\alpha]_D^{16}$ +6.9° (*c*=4.23, H_2O) (3.4 g, 0.029 mole) was treated in a similar manner to DL–X. The *S*–XI–HCl obtained by evaporation of the reaction mixture was reduced with 6 eq. of $NaBH_4$ in 75% aq. EtOH. The same treatment as in the case of DL–XI afforded a pale yellow oil (0.5 g, 18%), which was submitted to fractional distillation to give *S*(−)–XII as a colorless oil, bp 82—83° (24 mmHg), $[\alpha]_D^{13}$ −2.0° (*c*=4.088, EtOH). IR ν_{max}^{Cap} cm^{-1}: 3335, 3270, 1595, 1060. This infrared spectrum was identical with that of DL–XII.

Acid oxalate was prepared as colorless crystals, mp 168—168.5° (recrystallized from aq. EtOH), $[\alpha]_D^{17}$ −6.8° (*c*=1.416, H_2O). *Anal.* Calcd. for $C_7H_{15}O_5N$: C, 43.51; H, 7.83; N, 7.25. Found: C, 43.51; H, 7.53: N, 7.26. IR ν_{max}^{KBr} cm^{-1}: 3440, 3400, 1726, 1620, 1608, 1080, 1055. This infrared spectrum was different from that of DL–XII acid oxalate in the same state.

On the other hand, anhyd. *R*(−)–X($[\alpha]_D^{12}$ −5.4° (*c*=2.03, H_2O)) was treated in the same way as *S*(+)–X to afford *R*(+)–XII as a pale yellow oil (0.36 g, 11%), $[\alpha]_D^{15}$ +1.2° (*c*=7.21, EtOH) (lit.,[13] $[\alpha]_D^{25}$ +3.39° (26.547 g in 100 ml of EtOH)). The infrared spectrum of this sample was identical with that of *S*(−)–XII in the same state.

DL-4-Ethyl-4-methyl-2-oxazolidinone (DL-IX)——A mixture of DL–XII (2.8 g, 0.027 mole) and NaOMe (catalytic amount) in Et_2CO_3 (15.8 g, 0.134 mole) was refluxed for 4 hr and the EtOH generated was successively distilled off from the reaction mixture.[40] Evaporation to dryness *in vacuo* gave a viscous oil, which was submitted to fractional distillation to afford DL–IX as a colorless oil (2.7 g, 77%), bp 146—150° (5 mmHg). IR ν_{max}^{Cap} cm^{-1}: 3260, 1750, 1039. This oil solidified as a colorless solid with a low melting point when kept at room temperature. NMR (60 Mc, in CCl_4, TMS internal standard): 9.01 τ (3H, triplet, J=7.2 cps, $-CH_2-\underline{CH_3}$), 8.70 τ (3H, singlet, $-\underset{|}{\overset{|}{C}}-\underline{CH_3}$), 8.36 τ (2H, quartet, J=7.2 cps, $-\underline{CH_2}-CH_3$), 5.95 τ (2H, quartet, J=9.6 cps, $-O-\underline{CH_2}-\underset{|}{\overset{|}{C}}-$), 2.38 τ (1H, singlet, $-\underline{NH}-$). This nuclear magnetic resonance (NMR) spectrum was nearly equal to that reported by Smolinsky, *et al.*[13] The DL–IX thus obtained was confirmed as DL–XIII.

DL-3-Acetyl-4-ethyl-4-methyl-2-oxazolidinone (DL-XIII)——A mixture of DL–IX (0.70 g, 0.0054 mole) and anhyd. NaOAc (0.45 g, 0.0054 mole) in acetic anhydride (7 ml) was refluxed for 3 hr,[40] and then evaporated to dryness to afford a mixture of a white solid and oil. To the residue was added H_2O (10 ml) and the whole was extracted with ether (10 ml × 3). The ether layer was washed with satd. $NaHCO_3$ (10 ml × 1) and satd. NaCl (10 ml × 1), and dried over anhyd. Na_2SO_4. Filtration and evaporation gave a yellow oil, which solidified as a yellow solid (0.88 g, 95%), mp 48.5—51.5° (sintered at *ca.* 45°). Recrystallization from hexane (8 ml) gave DL–XIII as colorless needles (0.70 g, 76%), mp 50.5—52°. An analytical sample was prepared from several recrystallizations of the same solvent, mp 50—52°. *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.10; H, 7.42; N, 8.28. IR ν_{max}^{KBr} cm^{-1}: 1769, 1706, 1102. NMR (60 Mc, in CCl_4, TMS internal standard): 9.14 τ (3H, triplet, J=6.6 cps, $-CH_2-\underline{CH_3}$), 8.46 τ (3H, singlet, $-\underset{|}{\overset{|}{C}}-\underline{CH_3}$), 8.29—7.73 τ (2H, multiplet, $-\underline{CH_2}-CH_3$), 7.58 τ (3H, singlet, $-CO-\underline{CH_3}$), 5.95 τ (2H, quartet, J=8.4 cps, $-O-\underline{CH_2}-\underset{|}{\overset{|}{C}}-$).

***R*(+)-4-Ethyl-4-methyl-2-oxazolidinone (*R*(+)-IX)**——*R*(+)–XII ($[\alpha]_D^{15}$ +1.2° (*c*=7.21, EtOH)) (0.36 g, 0.0035 mole) was treated the same way as DL–XII to give *R*(+)–IX as a pale yellow viscous oil (0.30 g, 67%). This oil distilled out up to bp 123° (4 mmHg), $[\alpha]_D^{12}$ +1.0° (*c*=5.922, EtOH) (lit.,[13] $[\alpha]_D^{25}$ +0.354° (32.437 g in 100 ml of EtOH)). The infrared spectrum of this sample was identical with that of DL–IX. The optical purity of this *R*(+)–IX was assumed to be 45%, because no purification method other than distillation from *R*(−)–X to *R*(+)–IX was used. ORD: $[M]^{12}$ (*c*=5.922, EtOH) (mμ); +0.5° (700), +1.2° (589), +1.8° (500), +2.7° (450), +4.0° (400), +6.6° (350), +7.0° (347). *R*(+)–IX was confirmed as *R*(−)–XIII.

***R*(−)-3-Acetyl-4-ethyl-4-methyl-2-oxazolidinone (*R*(−)-XIII)**——The same treatment of *R*(+)-IX ($[\alpha]_D^{12}$ +1.0° (*c*=5.922, EtOH)) (0.27 g, 0.0021 mole) as in the case of DL-IX gave crude *R*(−)-XIII as a pale yellow oil (0.31 g, 87%), which solidified when kept at room temperature, mp 51.5—57° (sintered at 45°). Two recrystallization from hexane gave *R*(−)-XIII as colorless crystals, mp 56—61° (sintered at 50°), $[\alpha]_D^{12}$ −6.9° (*c*=2.064, EtOH). *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.11; H, 7.71; N, 8.22. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775, 1706, 1101. IR ν_{max}^{KBr} cm^{-1}: 1769, 1706, 1103. This infrared spectrum was identical with that of DL-XIII in its solid state. ORD: $[M]^{11}$ (*c*=2.064, EtOH) (mμ): −6.6° (700), −9.2° (589), −11.9° (500), −14.5° (450), −17.9° (400), −18.7° (366, neg. max.), −17.9° (350), 0° (308), +13.6° (300), +86.8° (284).

***S*(+)-2-Methylbutyl Azidoformate(*S*(+)-VIII)[13]**——*S*(−)-VIII (bp 128—129°, α_D^{19} −2.092° (*l*=0.5, neat), optical purity 84%)[43,45] (8.5 g, 0.097 mole) was added to stirred, cooled 12.5% benzene solution (100 g) of $COCl_2$ (12.5 g, 0.126 mole) maintained in a N_2 atmosphere. The whole was stirred for 30 min under ice cooling and a N_2 stream, and then for 4 hr, at room temperature. Evaporation of benzene *in vacuo* gave a pale yellow oil, which was added to aqueous MeOH (H_2O—MeOH 1:4, 50 ml) containing NaN_3 (7.0 g, 0.108 mole). The whole was stirred at room temperature for 15 hr. Petr. ether (100 ml) was added to the reaction mixture, and the organic layer was isolated. The aqueous layer was further extracted with petr. ether (50 ml×2) and the combined organic layer was washed successively with H_2O (50 ml×1), 10% Na_2CO_3 (50 ml×1) and H_2O (50 ml×1), and then dried with anhyd. Na_2SO_4. Filtration and careful evaporation gave *S*(+)-VIII as an oil (9.8 g, 64%), α_D^{11} +2.296° (*l*=0.5, neat) (lit.,[13] α_D^{21} +4.86° (*l*=1, neat), optical purity 77%). IR ν_{max}^{Cap} cm^{-1}: 2190 (sh), 2150, 1760, 1736, 1233. The *S*(+)-VIII obtained was immediately used without any purification for the following thermal decomposition.

Thermal Decomposition[13,46] of *S*(+)-2-Methylbutyl Azidoformate (*S*(+)-VIII)——To diphenyl ether (100 ml) preheated at 200° was added diphenyl ether solution (50 ml) of *S*(+)-VIII (α_D^{11} +2.296° (*l*=0.5, neat) (9.7 g, 0.062 mole) over a 10 min period in a N_2 atmosphere. The temperature of the reaction medium was kept at 200±10° during the addition of the diphenyl ether solution. Vigorous gas evolution occurred and the reaction mixture became brown. Stirring and heating were continued for an additional 10 min and then the whole was kept at room temperature overnight. Diphenyl ether solution was submitted to column chromatography with Al_2O_3 (pretreated with AcOEt) (100 g). After diphenyl ether was eluted with petr. ether, the eluting solvent was changed to $CHCl_3$. The fractions containing IX were found by using thin-layer chromatography (Al_2O_3, solvent $CHCl_3$ *Rf* value 0.4),[8] and combined. Evaporation of the combined fractions gave a reddish brown oil (1.84 g), which was twice distilled fractionally to afford a pale yellow oil (1.01 g), bp 105—138° (3 mmHg) (second distillation). The oil obtained was purified with column chromatography using silica gel (150 g, solvent AcOEt). The fractions containing only IX were found with thin-layer chromatography (silica gel, solvent AcOEt),[83] and combined. A yellow oil (0.58 g) obtained by evaporation of the combined fractions was submitted to fractional distillation to afford *R*(+)-IX as a pale yellow oil (0.56 g, 7.0%), bp 100—155° (10 mmHg), $[\alpha]_D^8$ +2.0° (*c*=11.068, EtOH) (lit.,[13] $[\alpha]_D^{25}$ +0.354° (32.437 g in 100 ml of EtOH)). IR ν_{max}^{Cap} cm^{-1}: 3260, 1750, 1038. This infrared spectrum was identical with that of DL-IX. Thin-layer chromatography (silica gel),[83] using two different solvent systems, showed single spots, whose *Rf* value was identical with the authentic DL-IX. *Rf* 0.7 (AcOEt), 0.2 ($CHCl_3$). ORD: $[M]^9$ (*c*=11.068, EtOH) (mμ): +1.3° (700), +1.9° (589), +3.2° (500), +4.5° (450), +7.0° (400), +13.8° (350), +14.9° (339). Since the optical purity of *R*(+)-IX obtained from *S*(+)-VIII became 90%, based on the optical purity of the authentic *R*(+)-IX prepared independently from *R*(−)-X, the percent of retention of thermal decomposition is calculated to be 107%.

R(+)-IX ($[\alpha]_D^8$ +2.0° (*c*=11.068, EtOH)) (0.52 g, 0.0040 mole) was treated the same as DL-IX[40] to afford a yellow oil (0.56 g, 82%), which solidified on stimulation. Three recrystallizations from hexane gave *R*(−)-XIII as colorless crystals, mp 72.5—74°, $[\alpha]_D^9$ −10.8° (*c*=1.834, EtOH). *Anal.* Calcd. for $C_8H_{13}O_3N$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.18; H, 7.61; N, 8.02. IR ν_{max}^{KBr} cm^{-1}: 1769, 1706, 1101. This infrared spectrum was identical with that of the authentic DL-XIII. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1777, 1707, 1101. This infrared spectrum was identical with that of *R*(−)-XIII prepared from *R*(−)-X in the same state. The mixed melting point with *R*(−)-XIII obtained from *R*(−)-X was mp 61—69°. ORD: $[M]^{10}$ (*c*=1.834, EtOH) (mμ): −12.9° (700), −16.7° (589), −19.6° (550), −23.8° (500), −28.9° (450), −34.9° (400), −38.0° (364, neg. max.), −37.1° (350), 0° (307), +25.2° (300), +288° (276).

DL-α-Methylphenylalanine Ethyl Ester (DL-XVIII)——To a suspension of DL-XVII[49,51] (15.0 g, 0.0838 mole) in EtOH (150 ml) was added $SOCl_2$ (49.7 g, 0.418 mole) dropwise with stirring and ice cooling (10—20°) for 15 min. The reaction mixture was refluxed and stirred for 6 hr. Evaporation *in vacuo* gave a pale yellow oil, which was dissolved in H_2O (100 ml). To the aqueous solution was added $NaHCO_3$ (7.1 g), and the whole was extracted with ether (50 ml×1). Addition of $NaHCO_3$ (7.1 g) and extraction with ether (50 ml×1) was repeated again. The aqueous layer was made further alkaline by the addition of conc. NaOH (5 g in H_2O (10 ml)) and extracted with ether (50 ml×2). Ether layers were combined, washed with satd. NaCl (50 ml×3), and then dried with anhyd. Na_2SO_4. Filtration and evaporation gave a yellow oil (15.3 g), which was submitted to fractional distillation to give DL-XVIII as a colorless oil (12.7 g, 74%), bp 134—

83) Spraying of conc. H_2SO_4 and then heating was used for coloring.

135° (12 mmHg) (lit.,[50] bp 152—154° (8—10 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3370, 3310, 1745, 1603, 1585, 1194, 1104, 765, 741, 702.

The hydrochloride was obtained as colorless prisms, mp 149.5—151.5° (recrystallized from EtOH–ether). *Anal.* Calcd. for $C_{12}H_{17}O_2N$–HCl: C, 59.13; H, 7.44; N, 5.75. Found: C, 59.05; H, 7.47; N, 5.88. IR ν_{max}^{KBr} cm^{-1}: 3250, 1740, 1733, 1603, 1572, 1233, 1220, 742, 705.

The neutral oxalate was prepared, as usual, as a colorless powder, mp 148.5—150° (recrystallized from EtOH—ether). *Anal.* Calcd. for $C_{26}H_{36}O_4N_2$: C, 61.89; H, 7.19; N, 5.55. Found: C, 62.06; H, 7.05; N, 5.81. IR ν_{max}^{KBr} cm^{-1}: 2980, 1750, 1622, 1603, 1582, 1300, 1225, 770, 755, 737, 702.

R(+)-α-Methylphenylalanine Ethyl Ester (R(+)-XVIII)——10% HCl (140 ml) containing R(+)-XXII[49,51] (mp 200—202°, $[\alpha]_D^{25}$ +75.0° (c=0.944, MeOH), optical purity 100%) was refluxed for 3 hr, and then evaporated to dryness to afford a white solid. Addition of H_2O (30 ml) to the residue and evaporation to dryness were twice repeated. The white solid obtained was treated in the same way as DL–XVII to give R(+)-XVIII as a colorless oil (5.3 g, 81%), bp 119—122° (7 mmHg), α_D^{23} +1.182° (l=0.1, neat), $[\alpha]_D^{23}$ +2.3° (c=3.020, EtOH). IR ν_{max}^{Cap} cm^{-1}: 3370, 3310, 1735, 1603, 1585, 1193, 1103, 765, 740, 701. This infrared spectrum was superimposable on that of DL–XVIII in the same state. The hydrochloride was too hygroscopic to examine.

The neutral oxalate was prepared as colorless plates, mp 154—154.5° (recrystallized from EtOH), $[\alpha]_D^{23}$ −12.1° (c=1.466, EtOH). *Anal.* Calcd. for $C_{26}H_{36}O_8N_2$: C, 61.89; H, 7.19; N, 5.55. Found: C, 61.84; H, 6.94; N, 5.43. IR ν_{max}^{KBr} cm^{-1}: 2980, 1754, 1625, 1585, 1535, 1300, 771, 756, 737, 700. This infrared spectrum was different from that of the racemic compound in the same state.

DL-2-Amino-2-methyl-3-phenylpropanol (DL-XIX)——A mixture of DL–XVIII (10.0 g, 0.0483 mole) and $NaBH_4$ (10.1 g, 0.266 mole) in 75% aq. EtOH (100 ml) was refluxed with stirring for 8 hr.[38] After being cooled, the reaction mixture was filtered and the precipitates washed with EtOH (40 ml). The combined filtrate and washings were concentrated to *ca.* 50 ml. Ether (50 ml) and H_2O (50 ml) was added to the concentrated aqueous solution. After addition of NaOH (1 g in H_2O (10 ml)), and saturation with NaCl of the lower aqueous layer, the ether layer was isolated. The aqueous layer was further extracted with ether (50 ml×3). The combined ether layers were washed with satd. NaCl (50 ml×1), and dried over anhyd. K_2CO_3. Filtration and evaporation under a N_2 atmosphere gave a pale yellow oil (7.7 g) to which was applied fractional distillation under a N_2 stream to afford DL–XIX as a colorless oil (5.7 g, 71%), bp 134—135° (6 mmHg). DL–XIX thus obtained solidified gradually when kept at room temperature, mp 92—93.5°. IR ν_{max}^{KBr} cm^{-1}: 3340, 3270, 1601, 1580, 1050, 729, 703. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 1603, 1583, 1040.

The hydrochloride was prepared as usual, as a colorless powder, mp 155.5—157.5° (recrystallized from EtOH–ether). *Anal.* Cacld. for $C_{10}H_{15}ON$–HCl: C, 59.54; H, 8.00; N, 6.94. Found: C, 59.38; H, 7.96; N, 6.88. IR ν_{max}^{KBr} cm^{-1}: 3210, 1613, 1603, 1584, 1510, 1072, 1051, 771, 733, 704.

The neutral oxalate was obtained as colorless plates, mp 267.5° (decomp.) (recrystallized from aq. EtOH). *Anal.* Calcd. for $C_{22}H_{32}O_6N_2$: C, 62.84; H, 7.67; N, 6.66. Found: C, 63.02; H, 7.65; N, 6.74. IR ν_{max}^{KBr} cm^{-1}: 3255, 1616, 1568, 1071, 1060, 783, 757, 724, 700.

R(+)-2-Amino-2-methyl-3-phenylpropanol (R(+)-XIX)——R(+)-XVIII (bp 119—122° (7 mmHg), α_D^{23} +1.182° (l=0.1, neat)) (4.5 g, 0.022 mole) was treated in the same way as DL–XVIII[38] to give a pale yellow oil (2.9 g, 81%), after evaporation of the ether extract, which gradually solidified, mp 68.5—73°, $[\alpha]_D^{24}$ +4.5° (c=1.408, EtOH). One recrystallization from a mixture of benzene and hexane (1:1) (50 ml) gave R(+)-XIX as colorless prisms (2.4 g, 67%), mp 72.5—75°, $[\alpha]_D^{25}$ +5.4° (c=0.956, EtOH). Further recrystallization of R(+)-XIX from benzene–hexane (1:1) afforded pure R(+)-XIX as colorless prisms, mp 72.5—74°, $[\alpha]_D^{21}$ +4.8° (c=1.336, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3335, 3275, 1603, 1584, 1072, 1060, 727, 701. This infrared spectrum was different from that of DL–XIX in a solid state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360, 1603, 1582, 1040. This infrared spectrum was identical with that of DL–XIX in the same state.

The hydrochloride was prepared as colorless needles, mp 140—141° (sintered at *ca.* 120°), (recrystallized form EtOH–ether), $[\alpha]_D^{25}$ +4.6° (c=1.528, EtOH). *Anal.* Calcd. for $C_{10}H_{15}ON$–HCl: C, 59.54; H, 8.00; N, 6.94. Found: C, 59.26; H, 7.77; N, 7.21. IR ν_{max}^{KBr} cm^{-1}: 3165, 1610, 1537, 1065, 1054, 770, 736, 702. This infrared spectrum was different from that of the racemic compound in a solid state. This hydrochloride was slightly hygroscopic.

The neutral oxalate was prepared as colorless plates, mp 263.5° (decomp.), $[\alpha]_D^{25}$ +14.8° (c=1.078, AcOH). *Anal.* Calcd. for $C_{22}H_{32}O_6N_2$: C, 62.63; H, 7.67; N, 6.66. Found: C, 62.63; H, 7.40; N, 6.72. IR ν_{max}^{KBr} cm^{-1}: 3410, 3250, 1613, 1571, 1549, 1060, 757, 724, 701. This infrared spectrum was different from that of the racemic neutral oxalate in the same state.

DL-4-Benzyl-4-methyl-2-oxazolidinone (DL-XVI)——A mixture of DL–XIX (1.2 g, 0.0073 mole) and NaOMe (catalytic amount) in diethyl carbonate (4.3 g, 0.036 mole) was refluxed for 4 hr[40] in the same manner as DL–IX. Evaporation of excess diethyl carbonate *in vacuo* afforded a mixture of a pale yellow oil and a solid, to which was added $CHCl_3$ (20 ml). The $CHCl_3$ layer was washed with satud. NaCl (10 ml×3), and dried with anhyd. Na_2SO_4. Filtration and evaporation gave DL–XVI as a white solid (1.3 g, 94%), mp 112—116°. One recrystallization from a mixture of benzene and hexane (2:1) (9 ml) afforded DL–XVI as colorless prisms (1.1 g, 79%), mp 117—118°. An analytical sample was prepared by several recrystallizations from benzene–hexane. Colorless prisms, mp 116.5—118°. *Anal.* Calcd. for $C_{11}H_{13}O_2N$: C, 69.09;

H, 6.85; N, 7.33. Found: C, 69.00; H, 6.75; N, 7.50. IR ν_{max}^{KBr} cm^{-1}: 3240, 1738, 1604, 1045, 751, 706. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3250, 1756, 1041. NMR (60 Mc, in $CDCl_3$, TMS internal standard): 8.68 τ (3H, singlet, $-\underset{|}{\overset{|}{C}}-CH_3$), 7.16 τ (2H, singlet, $-CH_2-C_6H_5$), 5.88 τ (2H, quartet, J=9 cps, $-O-CH_2-\underset{|}{\overset{|}{C}}-$), 3.09 τ (1H, singlet, $-NH-$), 2.78 τ (5H, singlet, benzene ring proton).

***R*(−)-4-Benzyl-4-methyl-2-oxazolidinone (*R*(−)-XVI)**——*R*(+)-XIX (mp 72.5—74°, $[\alpha]_D^{21}$ +4.8° (c=1.336, EtOH)) (1.2 g, 0.0073 mole) was treated in the same way as DL-XIX to afford a pale yellow oil (1.3 g), which partially solidified. One recrystallization of this oil, from a mixture of benzene and hexane (2:1) (9 ml), gave *R*(−)-XVI as colorless prisms (1.0 g, 72%), mp 98—100°, $[\alpha]_D^{23}$ −28.7° (c=0.830, EtOH). Several recrystallizations from benzene–hexane afforded an analytical sample of colorless prisms, mp 98—99.5°, $[\alpha]_D^{25}$ −28.8° (c=1.548, EtOH), $[\alpha]_D^{30}$ −28.3° (c=1.246, EtOH). This sample is 100% optically pure because the starting material XXII, already had an optical purity of 100%. *Anal.* Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.13; H, 6.67; N, 7.57. IR ν_{max}^{KBr} cm^{-1}: 3345, 1760, 1737, 1722, 1036, 752, 708. This infrared spectrum was different from that of DL-XVI in a solid state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3345, 3250, 1756, 1041. This infrared spectrum was identical with that of DL-XVI in the same state. ORD: $[M]^{24}$ (c=0.246, EtOH) (mμ): −34.2° (700), −49.7° (589), −68.5° (500), −93.2° (450), −118° (400), −169° (350), −237° (300), −349° (270).

DL-2-Methyl-3-phenylpropanol (DL-XXI)——To a suspension of $LiAlH_4$ (1.4 g, 0.037 mole) in ether (60 ml) was added an ether (25 ml) solution of DL-XX (5.0 g, 0.031 mole) under reflux and stirring.[52] Reflux and stirring were continued for 3 hr. A mixture of 12% NaOH (1.4 ml) and H_2O (4.2 ml) was added to the reaction mixture, and the precipitates were filtered and washed with ether. The combined ether layers were successively washed with satd. NaCl (20 ml×1), 10% Na_2CO_3 (20 ml×1), and satd. NaCl (20 ml×2), and then dried with anhyd. Na_2SO_4. Filtration and evaporation afforded a colorless oil, which was submitted to fractional distillation to give DL-XXI as a colorless oil (3.6 g, 78%), bp 111.5—113.5° (9 mmHg) (lit.,[53a] bp 77.5—78° (0.5 mmHg), bp 126—126.5° (15 mmHg); lit.,[53b] bp 245°; lit.,[53c] bp 128—129° (16 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3330, 1605, 1585, 1030, 739, 700.

3,5-Dinitrobenzoate was prepared by the treatment of DL-XXI with 3,5-dinitrobenzoyl chloride and pyridine. A pale yellow powder resulted, mp 58.5—60.5° (recrystallized from iso-Pr_2O). *Anal.* Calcd. for $C_{17}H_{16}O_6N_2$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.51; H, 4.68; N, 8.44. IR ν_{max}^{KBr} cm^{-1}: 1727, 1547, 1349, 1295, 1177, 745, 730, 718, 700. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1549, 1346, 1276, 1165.

***S*(−)-2-Methyl-3-phenylpropanol (*S*(−)-XXI)**——*S*(+)-XX (bp 146° (8.5 mmHg), α_D^{21} +1.939° (l=0.1, neat), optical purity 74%)[51] (9.0 g, 0.055 mole) was treated in the same way as DL-XX,[52] as described above, to afford *S*(−)-XXI as a colorless oil (5.4 g, 66%), bp 110.5—111.5° (9 mmHg), α_D^{23} −0.964° (l=0.1, neat), $[\alpha]_D^{24}$ −8.2° (c=4.632, benzene) (lit., [52a] bp 128° (16 mmHg), $[\alpha]_D^{26}$ +11.83°, d^{25} 0.980). IR ν_{max}^{Cap} cm^{-1}: 3340, 1605, 1585, 1033, 738, 700. This infrared spectrum was identical with that of DL-XXI in the same state.

3,5-Dinitrobenzoate was obtained from *S*(−)-XXI and recrystallized from iso-Pr_2O. Pale yellow crystals resulted, mp 79—81.5°, $[\alpha]_D^{24}$ +8.7° (c=1.196, benzene). *Anal.* Calcd. for $C_{17}H_{16}O_6N_2$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.13; H, 4.49; N, 8.31. IR ν_{max}^{KBr} cm^{-1}: 1725, 1545, 1349, 1295, 1178, 745, 731, 721, 700. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1736, 1550, 1347, 1276, 1165. These two infrared spectra were identical with those of the racemic compound in the same state respectively.

DL-2-Methyl-3-phenylpropyl Azidoformate (DL-XV)——DL-XXI (4.8 g, 0.032 mole) was treated the same as *S*(+)-VIII[13] to afford DL-XV as a pale yellow oil (6.9 g, 98%) when the dried petr. ether extract was evaporated. IR ν_{max}^{Cap} cm^{-1}: 2200 (sh), 2170 (sh), 2145, 1754, 1734, 1234, 739, 700. This oil was used immediately without any purification for thermal decomposition.

***S*(+)-2-Methyl-3-phenylpropyl Azidoformate(*S*(+)-XV)**——*S*(−)-XXI (bp 110.5—111.5° (9 mmHg), α_D^{23} −0.964° (l=0.1, neat)) (4.5 g, 0.030 mole) was converted to *S*(+)-XV (6.5 g, 98%) by the same treatment as in the case of DL-XV.[13] α_D^{21} +1.644° (l=0.1, neat). IR ν_{max}^{Cap} cm^{-1}: 2200 (sh), 2160 (sh), 2140, 1755, 1735, 1235, 740, 700. This infrared spectrum was superimposable on that of DL-XV in the same state. This oil was immediately applied to the following thermal decomposition.

Thermal Decomposition[13,46] of DL-2-Methyl-3-phenylpropyl Azidoformate(DL-XV)——To diphenyl ether (50 ml) preheated at 200±10° was added diphenyl ether solution (25 ml) containing DL-XV (6.9 g, 0.032 mole) with stirring and in N_2 atmosphere, for 10 min. The temperature of the reaction medium was kept at 200±10° during the addition of the diphenyl ether solution. The diphenyl ether solution was washed into the reaction mixture using an additional amount of diphenyl ether (5 ml), and further stirring was continued for 10 min at the same temperature. After standing at room temperature overnight, the whole was submitted to column chromatography using Al_2O_3 (pretreated with AcOEt) (300 g). Diphenyl ether was eluted from the column using petr. ether, and then the eluting solvent was changed to $CHCl_3$. Fractions, eluted by $CHCl_3$, containing DL-XVI were found with thin-layer chromatography (Al_2O_3, solvent $CHCl_3$ *Rf* value 0.3)[83] and combined. Evaporation of the combined fractions gave a reddish brown oil (1.54 g), to which distillation was applied to afford a yellow oil (0.78 g). This oil distilled out up to bp 194° (0.12 mmHg). This oil was purified again with column chromatography using silica gel (40 g, solvent hexane–AcOEt 1:1). Fractions containing only DL-XVI were identified from the thin-layer chromatography[83] (silica gel, solvent hexane–AcOEt 1:1) and combined using $CHCl_3$. DL-XVI obtained as a white solid (0.30 g, 5.0%) showed

a mp of 115—117°. Thin-layer chromatography (silica gel)[83] using two different solvent systems showed two single spots, respectively, whose *Rf* values were identical with those of the authentic DL–XVI. *Rf* 0.4 (hexane–AcOEt 1:1), 0.1 ($CHCl_3$). Twice recrystallizations from hexane–AcOEt afforded pure DL–XVI as colorless prisms, mp 116—117.5°. The mixed melting point with the authentic DL–XVI (mp 116.5—117.5°) showed no depression (mixed mp 116.5—118.5°). *Anal.* Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.95; H, 6.67; N, 7.47. IR ν_{max}^{KBr} cm^{-1}: 3245, 1737, 1605, 1046, 768, 708. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3250, 1756, 1041. These infrared spectra were identical with those of the authentic DL–XVI in the same state.

Thermal Decomposition[13,46] of *S*(+)-2-Methyl-3-phenylpropyl Azidoformate(*S*(+)-XV)——*S*(+)-XV (α_D^{21} +1.644° (*l*=0.1, neat)) (6.5 g, 0.030 mole) was treated in the same way as DL–XV to afford *R*(−)-XVI as a white solid (0.35 g, 6.2%), mp 85—100.5°, $[\alpha]_D^{24}$ −20.7° (*c*=1.586, EtOH). Thin-layer chromatography (silica gel)[83] using two different solvent systems showed single spots, respectively, whose *Rf* value were the same as those of the authentic DL–XVI. *Rf* 0.4 (hexane–AcOEt 1:1), 0.1 ($CHCl_3$). Gas chromatographic analysis of this solid showed a single peak whose retention time was identical with that of the authentic DL–XVI (10% SE-30 on Diasolid L, 3 m, 265°; retention time 4.6 min). The mixed melting point of this solid with the authentic *R*(−)-XVI (mp 99—99.5°) showed no depression (mp 92—96°). IR ν_{max}^{KBr} cm^{-1}: 3250, 1755, 1740, 1042, 765, 750, 705. This infrared spectrum was different from those of the authentic DL–XVI and *R*(−)-XVI in the same state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3240, 1757, 1042. This infrared spectrum was identical with those of the authentic DL–XVI and *R*(−)-XVI in $CHCl_3$ solution. The optical purity of this sample was calculated to be 72% based on the assumption that *R*(−)-XVI showing $[\alpha]_D^{25}$ −28.8° (*c*=1.548, EtOH) is optically pure.[55] It was evident that the percent of retention of configuration in this case was 97%. ORD: $[M]^{27}$ (*c*=0.220, EtOH) (mμ): −27.7° (700), −41.6° (589), −59.0° (500), −76.5° (450), −93.6° (400), −132° (350), −188° (300), −250° (270). Two recrystallizations from benzene–hexane afforded *R*(−)-XVI as colorless prisms, mp 87—107°. *Anal.* Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.82; H, 6.68; N, 7.52. $[\alpha]_D^{27}$ −20.2° (*c*=1.160, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3250, 1738, 1603, 1045, 765, 750, 705. This infrared spectrum was different from those of the authentic DL–XVI and *R*(−)-XVI in the same state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3240, 1757, 1041. This infrared spectrum was identical with those of the authentic DL–XVI and *R*(−)-XVI in the same state. The mixed melting point with the authentic *R*(−)-XVI (mp 99—100°) was mp 93—97°.

DL-, (+)-, and (−)-α-Methylphenylglycine (DL-, (+)-, and (−)-XXIII)——DL–XXIII was prepared from acetophenone[64,75] and resolved with quinine[56] through its N-formyl derivative.[41] Two lots of (+)-XXIII showing mp >250°, $[\alpha]_D^{25}$ +84.3° (*c*=0.976, N-HCl) and mp >250°, $[\alpha]_D^{18}$ +67.7° (*c*=0.910, N-HCl) were obtained. On the other hand, the (−)-XXIII prepared showed a mp >250°, $[\alpha]_D^{17}$ −70.0° (*c*=1.198, N-HCl) (lit.,[56] $[\alpha]_D^{18}$ +90.1° (N-HCl), $[\alpha]_D^{19}$ −90.3° (N-HCl)).

DL-α-Methylphenylgycine Ethyl Ester (DL-XXVI)——DL–XXIII (16.5 g, 0.10 mole) was treated in the same way as DL–XVII to afford an orange oil (15.9 g), to which was applied to fractional distillation to give DL–XXVI as a colorless oil (13.3 g, 69%), bp 120° (6.5 mmHg) (lit.,[66] bp 90—91° (1 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3380, 3310, 1734, 1602, 1232, 766, 701.

(+)-and (−)-α-Methylphenylglycine Ethyl Ester ((+)-and (−)-XXVI)——Crude (+)-XXIII (optical purity 82%)[69,84] (3.0 g, 0.018 mole) was treated in the same manner as DL–XXVI to afford (+)-XXVI as a colorless oil (2.2 g, 63%), bp 108—109.5° (5.5 mmHg), α_D^{16} +0.993° (*l*=0.1, neat) (lit.,[60] bp 144—146° (22 mmHg), α_D^{24} +12.14° (*l*=1, neat); lit.,[58] bp 69—70 (1mmHg), α_D^{25} +5.48° (*l*=0.5, neat)). IR ν_{max}^{Cap} cm^{-1}: 3370, 3300, 1733, 1603, 1235, 766, 701. This infrared spectrum was superimposable on that of the authentic DL–XXVI.

On the other hand, crude (−)-XXIII ($[\alpha]_D^{17}$ −70.0° (*c*=1.198, N-HCl)) (optical purity 78%)[69] was treated in the same way as (+)-XXIII to give (−)-XXVI as a colorless oil, bp 106—108° (4.5 mmHg), $\alpha_D^{24.5}$ −1.070° (*l*=0.1, neat), α_D^{16} −0.990° (*l*=0.1, neat). Since the maximum optical rotation of (+)-XXVI, α_D^{24} +12.14° (*l*=0.1, neat) was assumed to be 100% optically pure, (+)-XXVI exhibiting α_D^{16} +0.993° (*l*=0.1, neat) became 89% optically pure after the temperature difference was corrected.

DL-2-Amino-2-phenylpropanol (DL-XXVII)——A mixture of DL–XXVI (13.0 g, 0.0673 mole) and $NaBH_4$ (12.7 g, 0.336 mole) in 75% aq. EtOH (130 ml) was refluxed and stirred for 8 hr,[38] and then treated the same as in the case of DL–XIX to give DL–XXVII as a viscous oil (5.8 g, 57%), bp 140—144° (12 mmHg) (lit.,[65] bp 103—105° (1mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3335, 1603, 1062, 1047, 1029, 763, 701.

Hydrochloride was prepared as colorless prisms, mp 173—174° (decomp.) (recrystallized from EtOH–ether) (lit.,[65] mp 173—174° (decomp.)). IR ν_{max}^{KBr} cm^{-1}: 3140, 1615, 1044, 755, 694.

Neutral oxalate was obtained as colorless prisms, mp 217.5° (decomp.) (recrystallized from aq. EtOH). *Anal.* Calcd. for $C_{20}H_{26}O_6N_2$: C, 61.21; H, 7.19; N, 7.14. Found: C, 61.00; H, 7.00; N, 7.03. IR ν_{max}^{KBr} cm^{-1}: 3195, 1692, 1575, 1529, 1064, 755, 695.

84) Two lots of (+)-XXIII, $[\alpha]_D^{25}$ +84.3° (*c*=0.976, N-HCl) (1.14 g) and $[\alpha]_D^{18}$ +67.7° (*c*=0.910, 1N HCl) (1.86 g) were mixed and used directly, so that the optical purity of the mixture was calculated to be 82%.

(+)-2-Amino-2-phenylpropanol ((+)-XXVII)——(+)-XXVI (bp 108—109.5° (5.5 mmHg), α_D^{16} +0.993° (l=0.1, neat)) (2.1 g, 0.011 mole) was treated similarly to the case of DL-XXVII[38] to give (+)-XXVII as a colorless oil (1.2 g, 70%), bp 117—120.5° (4 mmHg), $[\alpha]_D^{23}$ +14.3° (c=0.978, EtOH). IR ν_{max}^{Cap} cm^{-1}: 3340, 1605, 1599, 1064, 1046, 1029, 763, 701. This infrared spectrum was identical with that of DL-XXVII in the state.

Neutral oxalate obtained as colorless needles showed mp 235° (decomp.) (recrystallized from aq. EtOH), $[\alpha]_D^{23}$ +7.0° (c=0.770, H_2O). *Anal.* Calcd. for $C_{20}H_{28}O_6N_2$: C, 61.21; H, 7.19; N, 7.14. Found: C, 61.45; H, 7.21; N, 7.37. IR ν_{max}^{KBr} cm^{-1}: 3150, 1650, 1603, 1519, 1053, 755, 697. This infrared spectrum was different from that of the racemic compound in the same state.

DL-4-Methyl-4-phenyl-2-oxazolidinone (DL-XXV)——The same treatment[40] of DL-XXVII (1.9 g, 0.013 mole) as in the case of DL-XVI afforded a pale yellow oil (2.3 g), which solidified when kept standing in an evacuated desiccator overnight. The solid showed mp 77.5—80.5°. Recrystallization from benzene–hexane afforded DL-XXV as colorless prisms (2.0 g, 87%), mp 81—82°. Further recrystallization from the same solvent gave DL-XXV as colorless prisms, mp 81.5—82.5° (lit.,[65] mp 79.6—80°). IR ν_{max}^{KBr} cm^{-1}: 3200, 1756, 1035, 762, 699. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 3240, 1760, 1042. NMR (60 Mc, in $CDCl_3$, TMS internal standard): 8.32 τ (3H, singlet, $-\underset{|}{\overset{|}{C}}-\underline{CH_3}$), 5.63 τ (2H, singlet, $-O-\underline{CH_2}-\underset{|}{\overset{|}{C}}-$), 2.64 τ (5H, singlet, benzene ring proton), 2.37 τ (1H, broad singlet, $-\underline{NH}-$).

(+)-4-Methyl-4-phenyl-2-oxazolidinone ((+)-XXV)——The same treatment[40] of (+)-XXVII (bp 117—120.5° (4 mmHg), $[\alpha]_D^{23}$ +14.3° (c=0.978, EtOH)) (0.56 g, 0.0037 mole), as in the case of DL-XXV, gave a pale yellow viscous oil (0.66 g), which was purified with column chromatography using silica gel (60 g, solvent $CHCl_3$). Fractions containing only (+)-XXV were found by thin-layer chromatography (silica gel, solvent $CHCl_3$, *Rf* value 0.1).[83] Evaporation of the solvent afforded pure (+)-XXV as a colorless oil (0.29 g), which solidified when kept at room temperature, mp 93—94.5°, $[\alpha]_D^{27}$ +101° (c=0.912, EtOH). The infrared spectrum of this sample was different from that of the authentic DL-XXV in a solid state, but identical to that in $CHCl_3$ solution. The optical purity of this (+)-XXV was assumed to be 89%, because no resolution of the racemic compound on the column chromatography with silica gel was expected. All the fractions containing (+)-XXV were combined (0.52 g) and recrystallized, twice, from benzene–hexane to give pure (+)-XXV as colorless plates, mp 93.5—94.5°, $[\alpha]_D^{24}$ +104° (c=0.894, EtOH). *Anal.* Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.91; H, 6.21; N, 8.11. IR ν_{max}^{KBr} cm^{-1}: 3260, 1765, 1719, 1043, 760, 679. This infrared spectrum was different from that of DL-XXV in the same state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 3240, 1757, 1042. This spectrum was superimposable on that of the authentic DL-XXV in $CHCl_3$ solution. ORD: $[M]^{19.2}$ (c=0.406, EtOH) (mμ): +140° (700), +209° (589), +287° (500), +365° (450), +489° (400), +733° (350), +1130° (300), +2000° (270).

DL-, *S*(+)-, and *R*(−)-Hydratropic Acid (DL-, *S*(+)-, and *R*(−)-XXIV)——DL-Hydratropaldehyde[67a] prepared from acetophenone was oxidized with $KMnO_4$[67b] to give DL-XXIV, bp 128.5—131° (5.5 mmHg) (lit.,[72] bp 161° (24 mmHg)). DL-XXIV was resolved with strychinine according to the method described by Raper.[72] The strychinine salt obtained was decomposed with Na_2CO_3 solution to afford *S*(+)-XXIV,[62] bp 125—126.5° (5.5 mmHg), $[\alpha]_D^{25}$ +52.2° (c=1.234, EtOH), optical purity 64%[71] (lit.,[72] $[\alpha]_D^{20}$ +81.1° (c=4.930, same EtOH); lit.,[63b] bp 123—124° (2.5—3.5 mmHg), $[\alpha]_D^{21}$ +98.9° (homog.), $[\alpha]_D^{21}$ +95.5° (c=3.5, benzene); lit.,[67b] bp 143° (12 mmHg), $[\alpha]_D$ +92.5° (c=3.4825, benzene)). The mother liquor of this resolution was similarly treated to give *R*(−)-XXIV,[62] bp 122—124° (4 mmHg), $[\alpha]_D^{24}$ −33.7° (c=4.930, EtOH), optical purity 42%.[71]

DL-2-Phenylpropanol (DL-XXVIII)——a) To a suspension of $LiAlH_4$ (1.0 g, 0.026 mole) in ether (60 ml) was added DL-hydratropaldehyde[67a] dropwise under reflux and stirring for 5 min. Reflux and stirring were continued for 3 hr[85] and the whole treated in the same manner as DL-XXI to afford DL-XXVIII as a colorless oil (6.7 g, 66%), bp 102—104° (10.5 mmHg) (lit.,[68a] bp 112—114 (12 mmHg); lit.,[68b] bp 110—112° (15 mmHg); lit.,[68c] bp 108—109° (14 mmHg)). IR ν_{max}^{Cap} cm^{-1}: 3340, 1603, 1033, 1013, 759, 700.

b) The same treatment of DL-XXIV, as in the case of XXI,[52] afforded DL-XXVIII as an oil (3.8 g, 64%), bp 101—103° (11 mmHg). The infrared spectrum of this sample was identical with that of DL-XXVIII prepared from DL-hydratropaldehyde.

DL-α-Naphthyl carbamate was prepared as usual, yielding colorless small needles, mp 103.5—104.5° (recrystallized from EtOH) (lit.,[68b] mp 100°; lit.,[68c] mp 100—101°). IR ν_{max}^{KBr} cm^{-1}: 3260, 1690, 1532, 786, 772, 706. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1732, 1527, 1494.

***R*(+)-2-Phenylpropanol (*R*(+)-XXVIII)**——*R*(−)-XXIV (bp 122—124° (4 mmHg), $[\alpha]_D^{24}$ −33.7° (c=4.930, EtOH) (6.2 g, 0.041 mole) was treated the same as DL-XXIV to afford *R*(+)-XXVIII as a colorless oil (4.0 g, 71%), bp 88—90 5° (5.5 mmHg), α_D^{24} +0.717° (l=0.1, neat), optical purity 40%[74] (lit.,[52b] bp 105—106° (11 mmHg), $\alpha_D^{25.5}$ +6.37±0.02° (l=2, neat); lit.,[73,86] bp not described, α_D^{20} +15.35° (l=1, neat)).

85) R.F. Nystrom and W.G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).
86) Eliel, *et al.* described that this optical rotation was not optically pure (see ref. 52b).

α-Naphthyl carbamate was obtained as colorless crystals, mp 102.5° (recrystallized from EtOH), $[\alpha]_D^{23}$ +5.9° (c=0.988, EtOH). *Anal.* Calcd. for $C_{20}H_{19}O_2N$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.87; H, 6.32; N, 4.58. IR ν_{max}^{KBr} cm^{-1}: 3260, 1688, 1530, 786, 772, 705. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1731, 1527, 1495. These infrared spectra were identical with those of the racemic compound in the same state.

DL-2-Phenylpropyl Azidoformate (DL-XXIX)——The same treatment of DL-XXVIII (6.2 g, 0.046 mole), as in the case of $S(+)$-VIII,[13] gave DL-XXIX as a colorless oil (8.4 g, 90%). IR ν_{max}^{Cap} cm^{-1}: 2190 (sh), 2150, 1755, 1730, 1231, 751, 700. The DL-XXIX obtained was used immediately for the following thermal decomposition.

***R*(+)-2-Phenylpropyl Azidoformate (*R*(+)-XXIX)**——$R(+)$-XXIX (5.2 g, 93%), α_D^{23} +0.222° (l=0.1, neat), was prepared from $R(+)$-XXVIII (bp 88—90.5° (5.5 mmHg), α_D^{24} +0.717° (l=0.1, neat)) by the same treatment as in the case of $S(+)$-VIII. This infrared spectrum was identical with that of DL-XXIX in the same state. This sample was applied immediately to the following step.

Thermal Decomposition[13,46] of DL-2-Phenylpropyl Azidoformate (DL-XXIX)——Diphenyl ether solution (35 ml) containing DL-XXIX (8.4 g, 0.041 mole) was added to stirred diphenyl ether (70 ml), preheated at 200°, and maintained in a N_2 atmosphere for 10 min. The temperature of the reaction mixture was kept constant. The diphenyl ether solution was washed into the reaction mixture using an additional amount of diphenyl ether (5 ml). Stirring, at 200±10°, was continued for 10 min. The reddish brown solution obtained was kept at room temperature overnight, and then submitted to column chromatography using Al_2O_3 (pretreated with AcOEt, 500 g). Diphenyl ether was eluted from the column using petr. ether, the eluting solvent was then changed to $CHCl_3$. Fractions containing DL-XXV were found and combined among those eluted with $CHCl_3$ by using thin-layer chromatography[83] (Al_2O_3, solvent $CHCl_3$ Rf value 0.35). The reddish brown oil (1.7 g) obtained was submitted to fractional distillation to afford a reddish orange oil (0.52 g). This oil distilled out up to bp *ca.* 175° (3 mmHg). This oil was purified again with column chromatography using silica gel (50 g, solvent, $CHCl_3$ and then AcOEt). Fractions which contained only DL-XXV were found using thin-layer chromatography[83] (silica gel, solvent $CHCl_3$ Rf value 0.15). These fractions were combined evaporated to dryness to give DL-XXV as a pale yellow oil (0.27 g, 3.7%), which solidified on trituration, mp and 77—79.5°. Several recrystall izations from benzene–hexane afforded pure DL-XXV as colorless crystals, mp 81.5—82.5°. The mixed melting point compared with that of the authentic DL-XXV (mp 81.5—82°) showed no depression (mixed mp 81.5—82.5°). IR ν_{max}^{KBr} cm^{-1}: 3200, 1755, 1035, 762, 699. This infrared spectrum was superimposable on that of the authentic DL-XXV in the same state.

Thermal Decomposition[13,46] of *R*(+)-2-Phenylpropyl Azidoformate (*R*(+)-XXIX)——$R(+)$-XXIX (α_D^{23} +0.222° (l=0.1, neat)) (5.2 g, 0.025 mole) was decomposed similar to the manner for DL-XXIX to afford (+)-XXV as a colorless oil (0.18 g, 4.0%), which solidified when kept at room temperature. mp 68.5—74.5°, $[\alpha]_D^{25}$ +43.9° (c=1.026, EtOH). The infrared spectrum of this sample, in a solid state, clearly demonstrated that this was contaminated with a fair amount of DL-XXV, but in $CHCl_3$ solution it was identical with those spectra of the authentic DL-XXV and (+)-XXV. The optical purity of this sample was assumed to be 39% based on the assumption that (+)-XXV showing $[\alpha]_D^{27}$ +101° (c=0.912, EtOH) was 89% optically pure. Then, the percent of retention of the configuration was calculated to be 93% or 98%.[77] Thin-layer chromatography[83] (silica gel) with two different solvent systems showed single spots, respectively, whose Rf values were identical with those of the authentic sample. Rf 0.2 ($CHCl_3$), 0.55 (hexane—AcOEt 1:1). Twice recrystallizations from benzene–hexane afforded (+)-XXV, with low optical purity, as white plates, mp 80.5—81.5°, $[\alpha]_D^{17}$ +9.3° (c=0.172, EtOH).[87] The mixed melting point with the authentic (+)-XXV (mp 93—94°) showed a mp 73.5—78°. *Anal.* Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.90; H, 6.43; N, 8.11. The infrared spectra of this sample were identical with those of the authentic DL-XXV in a solid state and in $CHCl_3$ solution. ORD: $[M]^{17}$ (c=0.172, EtOH) (mμ): +12.4° (700), +16.5° (589), +20.5° (500), +26.8° (450), +33.0° (400), +51.5° (350), +80.2° (300), +155° (270).

Photochemical Decomposition of *S*(+)-2-Methyl-3-phenylpropyl Azidoformate (*S*(+)-XV) and *S*(+)-2-Methylbutyl Azidoformate (*S*(+)-VIII)——1. Irradiation using low pressure mercury lamp.[88] a) (Table 2, run 3) CH_2Cl_2 (500 ml) solution containing DL-XV (2.00 g, 0.00913 mole) was irradiated internally in a N_2 atmosphere at *ca.* 10°, using a low pressure mercury lamp.[88] The whole was agitated with a N_2 stream from time to time. The irradiation was stopped after 8 hr, and the solvent was distilled off, under reduced pressure on the water bath maintained below 40°. The brown oil (2.0 g) obtained showed an almost complete absence of the starting material with thin-layer chromatography[83] (silica gel, solvent hexane–$CHCl_3$ 2:1). This oil was submitted to column chromatography using silica gel (150 g, solvent hexane–AcOEt 1:1). All the fractions which contained DL-XVI were found by using thin-layer chromatography[83] (silica gel, solvent hexane–AcOEt 1:1), and combined with $CHCl_3$. Evaporation of the $CHCl_3$ solution gave a yellow oil (0.50 g), which solidified when kept at room temperature. The infrared spectrum of this solid, in a solid state, was nearly identical with that of the authentic DL-XVI, and showed that this sample contained

87) This optical rotation was calculated from the optical rotatory dispersion chart.

88) A 30W low pressure mercury lamp with quartz protection tube manufactured by Rikosha, Ltd. was used.

no N_3 group. Distillation of this solid afforded a pale yellow solid (0.48 g), which distilled out up to bp 180° (0.1 mmHg). This oil solidified at room temperature. This solid was purified with column chromatography using silica gel (50 g, solvent hexane–AcOEt 1:1), and the fractions containing only DL–XVI were found, as before, and combined using $CHCl_3$. The nearly colorless oil obtained solidified to a very pale yellow solid (0.43 g, 25%), mp 115—116.5°. Infrared spectra of this sample were identical with those of the authentic DL–XVI in a solid state and in $CHCl_3$ solution. Thin-layer chromatography[83] (silica gel) with two different solvent systems showed single spots, respectively, whose *Rf* values were identical with those of the authentic sample. *Rf* 0.3 (hexane–AcOEt 1:1), 0.2 ($CHCl_3$). Recrystallization from benzene–hexane afforded DL–XVI as colorless prisms, mp 116—117°. The mixed melting point with the authentic sample (mp 116.5—117.5°) showed no depression (mixed mp 115.5—116.5°). Infrared spectra of this sample were superimposable on those of the authentic DL–XVI in a solid state and in $CHCl_3$ solution.

b) (Table 2, run 6). The same treatment of *S*(+)–XV (α_D^{29} +1.986° (*l*=0.1, neat), optical purity 84%)[89] (1.80 g, 0.00822 mole) as in the case of a) gave *R*(−)–XVI as a very pale yellow solid (0.42 g, 27%), mp 91—93.5°, $[\alpha]_D^{30}$ −24.1° (*c*=1.386, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3260, 1740, 1042, 750, 705. This infrared spectrum was different from those of the authentic DL–XVI and *R*(−)–XVI in the same state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3255, 1755, 1040. This infrared spectrum was identical with those of the authentic DL–XVI and *R*(−)–XVI in $CHCl_3$ solution. ORD: $[M]^{24}$ (*c*=0.236, EtOH) (mμ): −35.5° (700), −48.5° (589), −64.8° (500), −84.3° (450), −113° (400), −154° (350), −226° (300), −272° (270). Thin-layer chromatography using two different solvent systems showed single spots, respectively, whose *Rf* values were identical with those of the authentic DL–XVI. *Rf* 0.4 (hexane–AcOEt 1:1), 0.2 ($CHCl_3$). Gas chromatographic analysis of this sample showed a single peak whose retention time was identical with that of the authentic DL–XVI (10% SE-30 on Diasolid L, 3m, 265°; retention time 4.5 min). This sample seemed to be 85% optically pure based on the assumption that *R*(−)–XVI showing $[\alpha]_D^{30}$ −28.3° (*c*=1.246, EtOH) is 100% optically pure. The optical purity of the starting material was 84%, so that the percent of retention of the configuration was estimated to be 101%. Recrystallization from benzene–hexane gave *R*(−)–XVI as colorless crystals, mp 87.5—92°, $[\alpha]_D^{30}$ −22.7° (*c*=1.506, EtOH). This sample showed mp 92—97° on the mixed melting point with the authentic *R*(−)–XVI (mp 98—100°). IR ν_{max}^{KBr} cm^{-1}: 3240, 1735, 1044, 750, 701. This infrared spectrum was different from those of the authentic DL–XVI and *R*(−)–XVI measured in the same state. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3445, 3250, 1759, 1042. This infrared spectrum was identical with those of the authentic DL–XVI and *R*(−)–XVI in $CHCl_3$ solution.

c) (Table 2, run 7) CH_2Cl_2 (500 ml) solution containing *S*(+)–VIII (α_D^{30} +0.431° (*l*=0.1, neat), optical purity 86%[90]) (2.0 g, 0.013 mole) was treated in the same way as a) to afford *R*(+)–IX as a very pale yellow oil (0.50 g, 30%). The infrared spectrum of this sample, in capillary, was identical with that of the authentic sample. Thin-layer chromatography[83] (silica gel) showed a single spot whose *Rf* value was identical with that of the authentic DL–IX. *Rf* 0.7 (AcOEt). This oil was submitted to distillation to give *R*(+)–IX as a colorless oil (0.29 g), $[\alpha]_D^{15}$ +2.0° (*c*=3.544, EtOH). This oil distilled out up to bp 143° (6 mmHg). The optical purity of this sample was estimated to be 90% based on the assumption that *R*(+)–IX showing $[\alpha]_D^{12}$ +1.0° (*c*=5.922, EtOH) was 45% optically pure. From the above results, it was evident that the percent of retention of the configuration could be calculated as 105%.

The *R*(+)–IX obtained was acetylated as described before.[40] In this case, the crude *R*(−)–XIII prepared was purified with column chromatography using silica gel. *R*(−)–XIII obtained as a yellow solid showed a mp of 66.5—71.5°, $[\alpha]_D^{32}$ −10.7° (*c*=2.006, EtOH). Recrystallization from hexane gave *R*(−)–XIII as colorless prisms, mp 73.5—74.5°, $[\alpha]_D^{14}$ −11.1° (*c*=1.154, EtOH), whose infrared spectrum in a solid state was identical with that of *R*(−)–XIII as obtained in the case of thermal decomposition. The mixed melting point with *R*(−)–XIII, obtained previously in the case of thermal decomposition (mp 73—74°), showed no depression (mixed mp 72.5—74°).

2. Irradiation using a high pressure mercury lamp.[91] a) (Table 2, run 1) CH_2Cl_2 (500 ml) solution containing DL–XV (2.00 g, 0.00913 mole) was irradiated internally in a N_2 atomosphere at 10—21°, using a high pressure mercury lamp.[91] The irradiation was stopped after 2 hr.[92] Careful evaporation of the solvent, followed by the same purification methods as those used in the case of 1a), afforded DL–XVI as a colorless oil (0.21 g, 12%), which solidified when kept at room temperature, mp 113.5—116°. The DL–

89) This *S*(+)–XVI was prepared from *S*(+)–XX showing α_D^{24} +2.209° (*l*=0.1, neat), $[\alpha]_D^{25}$ +24.8° (*c*=4.508, benzene), bp 144—146.5° (7.5 mmHg). The optical purity of this *S*(+)–XX was calculated to be 84% based on the assumption that *S*(+)–XX showing $[\alpha]_D^{22}$ −24.56° (*l*=1, neat), d_4^{22} 1.065 was 100% optically pure.

90) This sample was obtained from *S*(−)–XIV, α_D^{30} −2.012° (*l*=0.5, neat), α_D^{20} −2.084° (*l*=0.5, neat), optical purity 86% (see ref. 45).

91) A 400W high pressure mercury lamp with Pyrex protection tube manufactured by Rikosha, Ltd. was used as the light source.

92) It was too difficult to keep the temperature of the reaction medium low for a long time because of the high temperature of the light source.

XVI obtained was identified the same way as 1a). Recrystallization from benzene–hexane gave DL–XVI as colorless prisms, mp 115.5—117°, which exhibited no depression (mixed mp 115.5—117°) on the mixed melting point with the authentic DL–XVI (mp 116—118°). This sample was also confirmed from infrared spectra and by thin-layer chromatography. (see 1b)). In this case, isolation of the unreacted starting material was not attempted.

b) (Table 2, run 4) $S(+)$–XV (α_D^{27} +2.201 (l=0.1, neat), optical purity 84%)[89] (2.0 g, 0.0091 mole) was treated as same as in the case of 2a) to afford a brown oil (2.0 g) which was submitted to column chromatography using silica gel (150 g, solvent hexane–AcOEt 1:1). Two fractions were obtained from the column chromatography, one of which, when eluted, contained mainly the unreacted starting material (1.3 g), and the other which was eluted later involved $R(-)$–XVI (0.35 g). The former fraction was purified using column chromatography with silica gel (100 g, solvent hexane–$CHCl_3$ 2:1) to afford $S(+)$–XV as a pale yellow oil (0.97 g, 49%), α_D^{24} +2.335° (l=0.1, neat). The infrared spectrum of this sample in capillary was identical with that of the authentic DL–XV. The latter fraction (0.35 g) was treated in a manner similar to 2a) to give $R(-)$–XVI as a pale yellow solid (0.24 g, 14%), mp 91.5—94°, $[\alpha]_D^{28}$ −24.8° (0.888, EtOH). This $R(-)$–XVI was confirmed by infrared spectra and by thin-layer chromatography (see 1b)). Gas chromatographic analysis of this sample demonstrated a single peak with the same retention time as that of the authentic DL–XVI (10% SE–30 on Diasolid L, 3m, 265°; retention time, 4.8 min). The optical purity of this sample was calculated to be 88% based on the assumption that $R(-)$–XVI showing $[\alpha]_D^{30}$ −28.3° (c=1.246, EtOH) was 100% optically pure.

The percent of retention of configuration was estimated to be 105%. Two recrystallizations from benzene–hexane gave pure $R(-)$–XVI as colorless plates, mp 86.5—89°, $[\alpha]_D^{27}$ −24.8° (c=0.912, EtOH). The mixed melting point with the authentic $R(-)$–XVI (mp 98.5—99.5°) showed mp 92—96°. This sample was also confirmed by infrared spectrum and by thin-layer chromatography.

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