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Synthesis of Aminohydroxy Acids from α-Amino Acids. Amino Acids XXXVII*

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A synthesis is described of the optically active α-hydroxy-β-amino acids VII, and of β-hydroxy-γ-amino acids VIII from optically active α-amino acids.

α-Hydroxy-β-amino acids were prepared from β-phthalimido-α-oxo acids IV. The preparation of these oxo acids started from phthalimido diazoketones obtained from α-amino acids[1] which were converted to bromoketones, and then converted using Kröhnke's synthesis through the pyridinium salts V into substituted nitriles VI. Hydrolysis of these nitriles afforded optically active β-phthalimido-α-oxo acids IV, which were converted through catalytic hydrogenation into β-phthalimido-α-hydroxy acids, and these further, by hydrolysis with hydriodic and acetic acids, into α-hydroxy-β-amino acids VII.

β-Hydroxy-γ-amino acids VIII were obtained by hydrolysing the phthalimido derivatives of vinylogous α-amino acids IX[4] with hydriodic and acetic acids.

Experimental conditions were investigated for the preparation of optically active pyridinium salts V under which no racemization nor Walden inversion occurred, and which was proved by the correlation of the configuration of α-oxo-β-phthalimidobutyric acid (IVa) and N-phthaloyl-L-alanine.

Earlier work in this laboratory has shown that optically active amino acids can be converted into their homologues I[1,2] and vinylogues II[3,4]. In addition we prepared, some years ago, the corresponding α-amino alkyl glyoxals III[5,6], starting with α-amino acids and using Kröhnke's procedure.[7] It was recently shown that the Kröhnke synthesis of α-oxo acids[8] can also be applied to derivatives of phthalimido acids,** and in this manner optically active β-phthalimido-α-oxo acids IV were obtained. Earlier prepared pyridinium salts V derived from L-alanine,[6] DL-valine[a] and *O*-methyl-L-tyrosine,[6] were condensed according to Kröhnke with *p*-nitrosodimethylaniline and sodium cyanide to α-(*p*-dimethylaminophenylimino)-β-oxo-γ-phthalimidonitriles VI. Compounds of the type VI were partially hydrolysed to α-oxo-β-phthalimido acids IV. Catalytic hydrogenation of IV and subsequent elimination of

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[a] D. Dvornik, *Thesis*, Faculty of Science, University of Zagreb, 1954.

the phthaloyl group gave very good yields of β-amino-α-hydroxy acids VII. The homologous γ-amino-β-hydroxy acids VIII can easily be prepared by acid hydrolysis of *N*-phthaloyl derivatives of vinylogous amino acids IX. The vinylogues IX were prepared by condensation of α-phthalimido aldehydes with malonic acid.[3,4]

$RCH(NH_2)CH_2CO_2H$ I

$RCH(NH_2)CH:CHCO_2H$ II

$RCH(NH_2)COC(=O)H$ III

$C_6H_4(CO)_2NCH(R)COCO_2H$ IV

$C_6H_4(CO)_2NCH(R)COCH_2NC_5H_5^{\oplus}\ Br^{\ominus}$ V

$C_6H_4(CO)_2NCH(R)COC(=NC_6H_4N(CH_3)_2\text{—}p)CN$ VI

$RCH(NH_2)CHOHCO_2H$ VII

$RCH(NH_2)CHOHCH_2CO_2H$ VIII

$C_6H_4(CO)_2NCH(R)CH:CHCO_2H$ IX

a, $R = CH_3$; b, $R = (CH_3)_2CH$; c, $R = (CH_3)_2CHCH_2$, d, $R = CH_3OC_6H_4CH_2\text{—}p$

Total synthetic methods for the preparation of aminohydroxy acids of the described type can give only mixtures of diastereoisomers. A preparation of β-amino-α-hydroxybutyric acid from crotonic acid has been described,[9] and evidently a mixture of stereoisomers was obtained. The same is the case with the synthesis of γ-amino-β-hydroxyvaleric acid.[10] It is therefore preferable to start with a natural amino acid.

As an example of this new preparation of amino-hydroxy acids, a description is given in this paper of the preparation of β-amino-α-hydroxy- and γ-amino-β-hydroxy acids derived from L-alanine.

The preparation of aminohydroxy acids from several other natural amino acids, especially from L-serine, is in progress, as well as the determination of their configuration.

EXPERIMENTAL

All melting points are uncorrected.

1-*Halo*-3-*phthalimidoalkan*-2-*ones* were prepared from the corresponding diazoketones. In the preparation of pyridinium salts, preferably bromoketones were used, but in our preliminary studies on the formation of optically active pyridinium salts chloro- and iodoketones were also used.

(*S*)-1-*Chloro*-3-*phthalimidobutan*-2-*one*[b] was prepared in the same manner as the corresponding bromo compound,[6] using concentrated hydrochloric acid instead of 48% hydrobromic acid. Colourless needles in a 96% yield were obtained which, recrystallized from dichloromethane-petroleum ether, showed the m. p. 120° and $[\alpha]_D^{18}$ —— 16° ±1° (c, 0.64 in acetone).

Anal. 9.01 mg. subst.: 18.92 mg. CO_2, 3.38 mg. H_2O

$C_{12}H_{10}O_3NCl$ (251.67) calc'd.: C 57.27; H 4.01%

found: C 57.32; H 4.20%

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[b] Specification of configuration is given in the recently proposed terms[11].

1-Iodo-3-phthalimidopropanone

1-Diazo-3-phthalimidopropanone (4 g.) was treated in the same manner as described in the preparation of methylketones from diazoketones,[12] but using one equivalent of 47% hydriodic acid. The amount of 4,5 g (76% yield) of colourless prisms of *1-iodo-3-phthalimidopropanone,* was obtained which after repeated recrystallization from acetone showed the constant m. p. 185°.

Anal. 14.39 mg. subst., 21.36 mg. CO_2, 3.17 mg. H_2O
$C_{11}H_8O_3NI$ (329.10) calc'd.: C 40.14; H 2.45%
found: C 40.51; H 2.47%

(S)-1-Iodo-3-phthalimido-4-(p-methoxyphenyl)-butan-2-one

A solution of 1-bromo-3-phthalimido-4-(*p*-methoxyphenyl)-butan-2-one (4.02 g., 0.01 mole $[\alpha]_D$ —200°) and sodium iodide (1.49 g.) in acetone (16 ml.) was left at 0° overnight. The sodium bromide was filtered off, the filtrate evaporated to dryness, and the crude (s)-*1-iodo-3-phthalimido-4-*(p-*methoxyphenyl)-butan-2-one* was obtained, yield 4.2 g. (95%). Recrystallization from ethyl acetate — petroleum ether gave colourless prisms, m. p. 118—120°, $[\alpha]_D^{16}$ —161° ± 1° (c, 1.28 in benzene).

Anal. 10.19 mg. subst.: 19.10 mg. CO_2, 3.38 mg. H_2O
$C_{19}H_{16}O_4NI$ (449.25) calc'd.: C 50.79; H 3.59%
found: C 51.15; H 3.71%

The pyridinium salts V derived from L-alanine (Va), L-leucine (Vc), and O-methyl-L-tyrosine (Vd) were prepared according to a modification of the earlier described procedure.[6] Our recent experience has shown that in the preparation of optically active pyridinium salts it is important to carry out the reaction of bromoketone with pyridine in acetone solution at 0°. In this manner optically pure compounds V could be prepared, from which keto-acids IV were obtained, showing the same configuration as the starting amino acids.

(*S*)-N-[*2-Oxo-3-phthalimidobutyl-(1)*]-*pyridinium bromide* (Va)

A solution of (S)-1-bromo-3-phthalimidobutan-2-one[6] (0.3 g.) in acetone (3 ml.) was treated with freshly distilled pyridine (1.2 ml.) at 0°. After standing for 2 hours the crystals of *(S)-N-[2-oxo-3-phthalimido-butyl-(1)]pyridinium bromide were* collected, yield 0.4 g. (94%), m. p. 85°, $[\alpha]_D^{23}$ —10° ± 0.5° (c, 1.08 in ethanol). (The earlier preparation gave $[\alpha]_D$ —8° for the pyridinium salt obtained by refluxing the bromoketone with pyridine.)

(S)-N-[5-Methyl-2-oxo-3-phthalimidohexyl-(1)]-pyridinium bromide (Vc) and *(S)-N-[4-*(p-*methoxyphenyl)-2-oxo-3-phthalimidobutyl-(1)]-pyridinium bromide* (Vd) were prepared in the same manner as the pyridinium salt Va and showed $[\alpha]_D^{16}$ —20° ± ± 2° (c, 0.30 in ethanol) and $[\alpha]_D^{17}$ —130° (c, 0.14 in ethanol) respectively. [The earlier preparation gave, for the compound Vc and Vd $[\alpha]_D$ —2° (unpublished) and $[\alpha]_D$ —83°[6] respectively.]

(*S*)-α-(p-*Dimethylaminophenylimino*)-β-*oxo*-γ-*phthalimido-valeronitrile* (VIa).

A solution of the pyridinium salt Va (1 g, $[\alpha]_D$ —10°) in 50% aqueous ethanol (4 ml.) was treated at room temperature with a solution of *p*-nitrosodimethylaniline (0.43 g.) in ethanol (8 ml.), and a solution of sodium cyanide (0.27 g) in water (1 ml.), according to Kröhnke[8]. On addition of the sodium cyanide separation of the dark red *(S)-α-(p-dimethylaminophenylimino)-β-oxo-γ-phthalimidovaleronitrile* occurred. Water (50 ml.), ethanol (10 ml.) and ether (10 ml.) were added, and the mixture left for a short time at 0°. The reaction product was filtered off, yield

0.85 g. (86%), m. p. 180°. Recrystallization from glacial acetic acid gave red needles with the m. p. 189°[c].

Anal. 9.89 mg. subst.: 24.33 mg. CO_2, 4.30 mg. H_2O
$C_{21}H_{18}O_3N_4$ (374.39) calc'd.: C 67.37; H 4.85%
found: C 67.12; H 4.86%

α-(p-Dimethylaminophenylimino)-β-oxo-γ-phthalimido-δ-methyl-capronitrile (VIb)

To a suspension of the pyridinium salt Vb derived from DL-valine[a] (3.65 g., 0.009 mole) in 50% aqueous ethanol (7 ml.) was added at room temperature a solution of *p*-nitrosodimethylaniline (1.3 g., 0.011 mole) in 50% ethanol (22 ml.). On addition of a solution of sodium cyanide (0.88 g., 0.018 mole) in water (3 ml.) a dark red precipitate of *α-(p-dimethylaminophenyl-imino)-β-oxo-γ-phthalimido-δ-methyl-capronitrile* separated. The reaction mixture was left at 0° for a short time, and the precipitate collected. Yield 2.9 g. (80%). Recrystallization from dioxane gave red prisms, m. p. 191°.

Anal. 9.76 mg. subst.: 24.48 mg. CO_2, 4.76 mg. H_2O
$C_{23}H_{22}O_3N_4$ (402.44) calc'd.: C 68.64; H 5.51%
found: C 68.46; H 5.46%

(S)-α-(p-Dimethylaminophenylimino)-β-oxo-γ-phthalimido-ε-methylenanthonitrile (VIc)

The pyridinium salt Vc (6.25 g., $[\alpha]_D$ —20°) was treated in the same manner as described in the preparation of the compound VIb. *(S)-α-(p-Dimethylamino-phenyl-imino)-β-oxo-γ-phthalimido-ε-methylenanthonitrile* was obtained, yield 3 g. (48%), m. p. 145—146°. Recrystallization from dichloromethane — petroleum ether gave thin purple needles, m. p. 151—152°.

Anal. 8.76 mg. subst.: 22.27 mg. CO_2, 4.54 mg. H_2O
$C_{24}H_{24}O_3N_4$ (416.42) calc'd.: C 69.21; H 5.81%
found: C 69.37; H 5.80%

(S)-α-(p-Dimethylaminophenylimino)-β-oxo-γ-phthalimido-δ-(p-methoxyphenyl) valeronitrile (VId)

The pyridinium salt Vd (1.44 g., 0.03 mole, $[\alpha]_D$ —130°) was treated in the same manner as described in the preparation of the compound VIb. *(S)-α-(p-Dimethyl-aminophenylimino)-β-oxo-γ-phthalimido-δ-(p-methoxyphenyl) valeronitrile* was obtained, yield 0.8 g. (56%), m. p. 130°. After recrystallization from ethyl acetate — petroleum ether, purple crystals were obtained, with the m. p. 141°.

Anal. 9.79 mg. subst.: 25.03 mg. CO_2, 4.48 mg. H_2O
$C_{28}H_{24}O_4N_4$ (480.51) calc'd.: C 69.99; H 5.03%
found: C 69.76; H 5.13%

L-*α-Oxo-β-phthalimidobutyric acid* (IVa)

To a suspension of (S)-α-(p-dimethylamino-phenylimino)-β-oxo-γ-phthalimido-valeronitrile (VIa, 1 g.) in glacial acetic acid (35 ml.), 4*N* hydrochloric acid was added (100 ml.) and the reaction mixture stirred for one hour at room temperature. The resulting clear solution was evaporated to dryness *in vacuo* (at a temperature not above 40°). The oily residue was treated with water (10 ml.) and extracted in the usual manner with ether. After evaporation of the ether, the oily L-*α-oxo-β-phthalimidobutyric acid* remained (0.66 g., 52%) which crystallized on standing.

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[c] Preparation of the same compound (m. p. 184—185°) from DL-alanine was recently described[13].

Recrystallization from ether — petroleum ether gave colourless needles, m. p. 178°, $[\alpha]_D^{19}$ $-18.5° \pm 0.5°$ (c, 1.76 in ethanol). For analysis the compound was sublimed at 140°/0.014 mm.

Anal. 10.60 mg. subst.: 22.72 mg. CO_2, 3.51 mg. H_2O
$C_{12}H_9O_5N$ (267.20) calc'd.: C 58.30; H 3.67%
found: C 58.51; H 3.71%

Proof of Configuration of L-*α-Oxo-β-phthalimido-butyric Acid.*

A solution of L-α-oxo-β-phthalimidobutyric acid (IVa, 0.3 g., $[\alpha]_D$ — 14°) in acetone (3 ml.) was treated at room temperature with Jones' chromic acid reagent (8*N* based on active oxygen, 0.16 ml.)[14]. After shaking the reaction mixture at room temperature for one hour, it was diluted with water and extracted with ether. The ethereal extracts were dried (sodium sulphate) and evaporated *in vacuo*. The resulting *N*-phthaloyl-L-alanine (0.16 g. 57.3%) showing $[\alpha]_D$ — 12° was recrystallized from ethyl acetate — petroleum ether to the constant m. p. 159—160°. Colourless prisms showing $[\alpha]_D^{24}$ $-20° \pm 0.9°$ (c, 1.05 in ethanol) were obtained. (Fischer[15] reported m. p. 150—152° and $[\alpha]_D^{18}$ — 17.5°.)

Anal. 6.92 mg. subst.: 15.27 mg. CO_2, 2.69 mg. H_2O
$C_{11}H_9O_4N$ (219.19) calc'd.: C 60.27; H 4.14%
found: C 60.21; H 4.34%

The compound gave no depression of melting point with an authentic specimen of *N*-phthaloyl-L-alanine.

L-*α-Oxo-β-phthalimidobutyric acid ethylene thioketal*

A mixture of L-α-oxo-β-phthalimidobutyric acid (0.3 g.), ethanedithiol (1.2 ml.) and boron fluoride etherate as catalyst (1.2 ml.)[16,d] was left at room temperature for 5 minutes. Ether (5 ml.) was then added, and the reaction mixture evaporated to dryness below 50°. A red oily residue of L-*α-oxo-β-phthalimidobutyric acid ethylene thioketal* was filtered through a column of alumina (1:5), and a colourless oil was obtained by evaporation of the filtrate. Yield 0.34 g. (77%) of colourless prisms, which after recrystallization from dichloromethane showed the m. p. 149—150° and $[\alpha]_D^{17}$ $+25° \pm 3°$ (c, 0.69 in dichloromethane).

Anal. 10.32 mg. subst.: 19.58 mg. CO_2, 3.87 mg. H_2O
$C_{14}H_{13}O_4NS_2$ (323.37) calc'd.: C 51.99; H 4.14%
found: C 51.78; H 4.20%

α-Oxo-β-phthalimido-γ-methylvaleric acid (IV b)

A mixture of α-(*p*-dimethylaminophenylimino)-β-oxo-γ-phthalimido-δ-methylcapronitrile (VIb, 1 g.), glacial acetic acid (40 ml.), and hydrochloric acid (4*N*, 50 ml.) was heated in a water-bath for 1 hour. From the reaction mixture the crude *α-oxo-β-phthalimido-γ-methylvaleric* acid was isolated in the same manner as described for IVa. Yield 0.4 g. (59%) of colourless needles, which after several recrystallizations from dichloromethane-petroleum ether showed the m. p. 129—131°.

Anal. 8.03 mg. subst.: 17.99 mg. CO_2, 3.54 mg. H_2O
$C_{14}H_{13}O_5N$ (275.25) calc'd.: C 61.09; H 0.76%
found: C 61.14; H 4.93%

L-*α-Hydroxy-β-phthalimidobutyric acid*

A solution of crude L-α-oxo-β-phthalimidobutyric acid (IVa) in acetone was filtered prior to hydrogenation through a column of alumina (1:5). After evaporating the solvent to dryness the purified compound IVa was obtained. Hydrogenation of

[d] Usual techniques for the preparation of thioketals failed in this case.

IVa (1.1 g.) was carried out over Adams' PtO_2 catalyst (100 m..) in ethanol (25 ml.) at atmospheric pressure and 18°. In 7 hours 1.1 mole of hydrogen was absorbed. The catalyst was filtered off, the filtrate evaporated to dryness and an oily residue of L-α-*hydroxy*-β-*phthalimidobutyric acid*[e] obtained, yield 1.1 g., which showed $[\alpha]_D^{20}$ + 31° ± 1° (c, 0.8 in ethanol). For analysis the compound was distilled at 400/0.02 mm. The colourless oil had the $[\alpha]_D$ unchanged.

Anal. 7.35 mg. subst.: 15.48 mg. CO_2, 2.94 mg. H_2O
$C_{12}H_{11}O_5N$ (249.22) calc'd.: C 57.83; H 4.45%
found: C 57.44; H 4.47%

L-β-*Amino*-α-*hydroxybutyric acid* (VII a)

To a solution of L-α-hydroxy-β-phthalimidobutyric acid (1 g., $[\alpha]_D$ + 31°) in glacial acetic acid (30 ml.) hydriodic acid was added (5.5 ml., 40%) and the resulting mixture refluxed for 8 hours. After cooling crystals of phthalic acid separated. The filtrate was evaporated to dryness under reduced pressure, the residue dissolved in water, and extracted with ether. The aqueous layer was again evaporated to dryness, the residue dissolved in distilled water (400 ml.) and passed through a column of Amberlite IR-4B (25 g.) at a flow rate of 400 ml./hr. Evaporation of the filtrates gave needles of crude L-β-*amino*-α-*hydroxybutyric acid*[e], yield 0.40 g. (87%), showing $[\alpha]_D^{20}$ + 5.0° ± 0.1° (c, 4.77 in water). Crystallization from methanol gave colourless needles with the m. p. 244° (decomp.), $[\alpha]_D$ unchanged.

Anal. 8.86 mg. subst.: 13.18 mg. CO_2, 6.08 mg. H_2O
2.18 mg. subst.: 0.227 ml. N_2 (18.7°, 747 mm.)
$C_4H_9O_3N$ (119.12) calc'd.: C 40.33; H 7.62; N 11.76%
found: C 40.61; H 7.68; N 11.98%

The optically inactive compound was prepared earlier by Neuberg[9] from crotonic acid.

L-γ-*Amino*-β-*hydroxyvaleric acid* (VIII a)

(+)-4-Phthalimido-2-pentenoic acid (IXa, 4 g.) prepared earlier[4] was treated with concentrated hydrochloric acid (40 ml.) in the same manner as described for the preparation of γ-amino-β-hydroxybutyric acid[3]. Subsequent evaporation *in vacuo*, and treatment with Amberlite IR-4B afforded L-γ-*amino*-β-*hydroxyvaleric acid*, yield 0.7 g. (41%), with the m. p. 177° and showing $[\alpha]_D^{16}$ + 4.7° ± 0.1° (c, 0.84 in water). Crystallization from water-ethanol gave colourless prisms with the m. p. 182°, and showing $[\alpha]_D^{18}$ + 5.7° ± 0.6° (c, 1.57 in water).

Anal. 10.02 mg. subst.: 16.58 mg. CO_2, 7.34 mg. H_2O
$C_5H_{11}O_3N$ (133.15) calc'd.: C 45.10; H 8,33%
found: C 45.13; H 8.20%

The optically inactive compound was prepared earlier by Osterberg[10] from laevulinic acid.

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IZVOD

Sinteza amino-oksi kiselina iz α-amino kiselina. Amino kiseline XXXVII

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Opisano je priređivanje optički aktivnih α-oksi-β-aminokiselina VII, kao i β-oksi-γ-aminokiselina VIII iz optički aktivnih α-aminokiselina.

α-Oksi-β-aminokiseline priređene su iz β-ftalimido-α-oksokiselina IV. Kod priređivanja tih ketokiselina polazilo se od ftalimido diazoketona dobivenih iz α-aminokiselina[1], koji su pretvoreni u bromketone, te dalje Kröhnkeovom sintezom[8], putem piridinijskih soli V, u supstituirane nitrile VI. Hidrolizom tih nitrila dobivaju se optički aktivne β-ftalimido-α-oksokiseline IV; katalitičkim hidriranjem one prelaze u β-ftalimido-α-oksikiseline, koje dalje prelaze, hidrolizom s jodovodičnom i octenom kiselinom, u α-oksi-β-aminokiseline VII.

Da se dobije β-oksi-γ-aminokiselina VIII, podvrgnuti su ftalimido derivati vinilognih α-amino-kiseline IX[4] hidrolizi s jodovodičnom i octenom kiselinom.

Za pripravljanje optički aktivnih piridinijskih soli V razrađeni su eksperimentalni uvjeti, koji ne uzrokuju racemizaciju ni eventualni Waldenov premještaj, što je utvrđeno korelacijom konfiguracija α-okso-β-ftalimidomaslačne kiseline (IVa) i *N*-ftaloil-L-alanina.

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