(1965); (b) F. Bohlmann, E. Winterfeldt, P. Studt, H. Laurent, G. Boroschewski, and K.-M. Kleine, *Chem. Ber.*, **94**, 3151 (1961).
(9) M. Uskokovic, H. Bruderer, C. von Planta, T. Williams, and A. Brossi, *J. Am. Chem. Soc.*, **86**, 3364 (1964).
(10) In order to exist as stable, separable, cis and trans conformers, a substituent(s), able to markedly inhibit the rate of inversion or provide a steric barrier to the process, would be required. However, no such substituent is known.
(11) T. Takemoto, Y. Kondo, and K. Kondo, *Yakugaku Zasshi*, **83**, 162 (1963).
(12) T. Kametani, M. Ihara, K.Fukumoto, H. Yagi, H. Shimanouchi, and Y. Sasada, *Tetrahedron Lett.*, 4251 (1968).
(13) A. H. Reine and A. I. Meyers, *J. Org. Chem.* **35**, 554 (1970).
(14) C. Schöpf and M. Schweickert, *Chem. Ber.*, **98**, 2566 (1965).
(15) R. E. Brown, A. I. Meyers, L. M. Trefonas, R. L. R. Towns, and J. N. Brown, *J. Heterocycl. Chem.*, **8**, 279 (1971).
(16) In another case, G. Van Binst and J. C. Nouls, *J. Chem. Soc. C*, 150 (1970), reported stable cis and trans species in the NMR spectrum. These results, however, should be reinvestigated.
(17) An erroneous assignment of another type has been made by T. Matsunaga, I. Kawasaki, and T. Kaneko, *Tetrahedron Lett.*, 2471 (1967), who report the synthesis of the diastereoisomers of 4-phenylquinolizidin-2-ol. Only two of the four isomers are correctly assigned, however, because configurational assignments IIA and IIC (also, IIB and IID) actually depict a *d* and *l* pair of a single diastereoisomer, each in a different conformation.
(18) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Am. Chem. Soc.*, **89**, 1431 (1967).
(19) F. Bohlmann, *Chem. Ber.*, **91**, 2157 (1958).
(20) H. S. Aaron, *Chem. Ind. (London)*, 1338 (1965).
(21) H. S. Aaron, G. E. Wicks, Jr., and C. P. Rader, *J. Org. Chem.*, **29**, 2248 (1964).
(22) H. S. Aaron, C. P. Rader, and G. E. Wicks, Jr., *J. Org. Chem.*, **31**, 3502 (1966).
(23) H. S. Aaron and C. P. Ferguson, *Tetrahedron*, **30**, 803 (1974).
(24) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York, N.Y., 1965: (a) p 237; (b) p 44; (c) p 252.
(25) (a) J. P. Ferris, R. C. Briner, and C. B. Boyce, *J. Am. Chem. Soc.*, **93**, 2953 (1971); (b) E. Fujita and Y. Saeki, *J. Chem. Soc., Perkin Trans. 1*, 297 (1973).
(26) J. A. Hamilton and L. K. Steinrauf, *J. Am. Chem. Soc.*, **93**, 2939 (1971).
(27) This value refers to the difference between the trans and a single cis-fused form. For unsubstituted quinolizidine, the presence of two equivalent cis-fused forms would result in an entropy of mixing factor (R ln 2) that would reduce this value by 0.4 kcal/mol at 25°, with reference to the total system.
(28) K. Winterfeld and H. R. Rath, *Arch. Pharm. (Weinheim, Ger.)*, **293**, 141 (1960); *Chem. Abstr.*, **60**, 522*e* (1964); **54**, 1739*e* (1960).
(29) Adapted from a cognate procedure of W. A. Reckhow and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 4960 (1952).
(30) Adapted from a cognate procedure of S. Archer, *J. Org. Chem.*, **16**, 430 (1951).
(31) C. P. Rader, G. E. Wicks, Jr., R. L. Young, Jr., and H. S. Aaron, *J. Org. Chem.*, **29**, 2252 (1964).
(32) At 250° on a 9 ft × 0.25 in. column of Carbowax 20M (13%) on Gas-Chrom P (60/80) at 85 ml/min He flow. The retention times (minutes) follow: **1**, 13.5; **2**, 18.7; **3**, 22.0; **4**, 26.3.

Some Reactions of DL-*trans*-4,5-Dicarbomethoxy-2-phenyl-2-oxazoline

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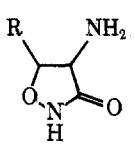
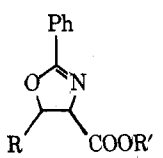
The synthesis and some anomalous reactions of the title compound (**4**) are discussed. Treatment of **4** with hydroxylamine caused oxazoline ring opening to form the amidoxime **5**. When the diester **4** was saponified, the *O*-benzoyl zwitterion **6** crystallized from solution in excellent yield. The structure of **6** was secured by its rearrangement into DL-*threo*-*N*-benzoyl-β-hydroxyaspartic acid (**10**) and its conversion into DL-*threo*-β-hydroxyaspartic acid dimethyl ester. In contrast, the oxazoline ring in monoester **2** (R = H; R′ = CH_3) is stable to both hydroxylamine and alkali.

We have been interested in the synthesis of derivatives and analogs of the antibiotic cycloserine (**1**, R = H) for many years. Recently, we have been working toward the synthesis of a 5-carbamido analog (**1**, R = $CONH_2$) of cycloserine, since this compound might reasonably be expected to inhibit asparagine synthetase. Since the original synthesis[1] of cycloserine proceeded through an oxazoline intermediate, **2** (R = H), we decided to investigate a synthetic scheme using the oxazoline dicarboxylic acid (**2**, R = COOH; R′ = H).

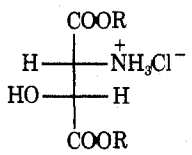


1



2

The starting material for this approach was β-hydroxyaspartic acid, the synthesis and stereochemistry of which we had investigated previously.[2] Esterification of the threo amino acid (**3**, R = H) followed by conversion of the ester into the oxazoline (**4**, R = CH_3) by reaction with ethyl benzimidate[3] was uneventful. The oxazoline ester was a crystalline compound, which was unstable at ambient temperatures but could be kept indefinitely in a refrigerator.



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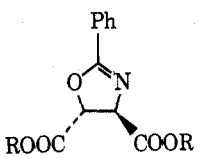
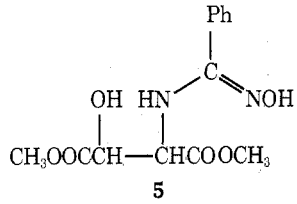


4

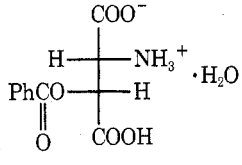
The difficulties with the oxazoline approach to **1** (R = $CONH_2$) began when attempts were made to convert the oxazoline ester into the corresponding dihydroxamic acid (**4**, RO = NHOH). The use of the standard methods of hydroxamic acid synthesis, i.e., treatment of the diester with at least 2 equiv of hydroxylamine in basic or neutral solution,[4] gave only highly colored products of a polymeric nature. All attempts to crystallize salts of the desired product from the mixture failed. Treatment of the crude product with ethanolic cupric acetate followed by isolation of the precipitated salts and liberation of the organic conjugate acids with hydrogen sulfide gave only tarry products. When, however, **4** was treated with 1 equiv of methanolic hydroxylamine, a white crystalline product, $C_{13}H_{16}N_2O_6$, was obtained in yields of 35–71%. The empirical formula indicated that 1 mol of oxazoline had combined with 1 mol of hydroxylamine. Significantly, the ester functions of the starting material were still present in this product as shown by infrared, NMR, and ^{13}C NMR spectroscopy. It gave a negative $FeCl_3$ test, but showed positive Tollens and Griess[5] tests indicating the presence of a reducing group, probably –NHOH or =NOH, in the molecule. Of all the possible structures considered, only the amidoxime structure **5** was consistent with all the spectral and chemical data. Importantly, when the proton decoupled ^{13}C NMR spectrum of the ester **4** (R = CH_3) was compared with that of the unknown compound, a signal at 152.2 ppm in the

spectrum of the latter had to be assigned to the carbon atom which had appeared at the 2 position in the oxazoline ring. This chemical shift is too far upfield for a carbonyl or oxazoline carbon atom, but was very close to the amidoxime carbon in benzamidoxime (150.8 ppm). These data, thus, confirmed the structure **5** for that of the hydroxylamine adduct. The reaction of imino esters with hydroxylamine to form amidoximes has been reported,[6] but, to our knowledge, the conversion of an oxazoline (cyclic imino ester) into an amidoxime has not been reported. This specific case of amidoxime formation seems to us even more unexpected in light of the conversion by hydroxylamine of the oxazoline ester (**2**, R = H; R′ = CH_3) into a hydroxamic acid in excellent yield.[4] It is difficult to understand why the presence of the 5-carbomethoxy group should cause the results of this reaction to be so completely different.



5

The enhanced reactivity of **4** at C-2 is reflected also in the opening of the oxazoline ring in the saponification of **4**. The acid obtained on acidification crystallized as a hydrate[7] which on drying lost 1 mol of water. The spectral and analytical data and a positive ninhydrin reaction indicated that the acid was not the expected oxazoline **4** (R = H), but rather DL-*threo*-*O*-benzoyl-β-hydroxyaspartic acid monohydrate (**6**). This structure was consistent with the fact that when **6** was treated with thionyl chloride at room temperature, a hydrochloride (**7**) rather than an oxazoline



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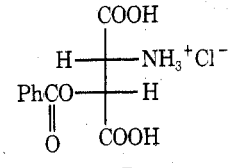
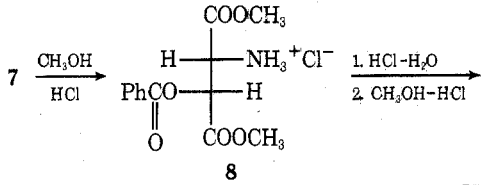


7

acid chloride hydrochloride was obtained. Dilute bicarbonate converted **7** back to **6** in excellent yield. The structure and configuration of **7** was confirmed by its conversion to the known DL-*threo*-β-hydroxyaspartic acid dimethyl ester hydrochloride[2,8] (**9**). Direct methanolysis of **7** to **9** failed



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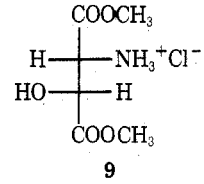

9

when it was found that **8** was the only product. Surprisingly, **8** was stable to refluxing saturated methanolic hydrogen chloride for 5 days. It was necessary to *hydrolyze* **8** to the crude acid and subsequently to convert the acid into the ester **9**. This extreme difficulty of ester methanolysis is reminiscient of difficulty experienced in the acid hydrolysis of an α-amino acetal in which the proximity of the positively charged amino function presumably retarded the reaction.[9] The fact that the threo ester (**9**) was finally obtained shows that no inversion of configuration had occurred in the formation of the acid **6** from **4**. One of the most interesting aspects of the acid **6** was its slow (72 hr) conversion in Me_2SO-d_6 into DL-*threo*-*N*-benzoyl-β-hydroxyaspartic acid (**10**). Both **10** and its erythro isomer were synthesized by benzoylation of the amino acids for spectral comparison with the rearrangement product. This is an example of a very slow O → *N*-acyl migration under very mildly basic (Me_2SO solution) conditions. In fact, when **6** was allowed to stand in aqueous basic solution overnight, **10** was obtained in excellent yield.

The fact that the oxazoline ring in **4** (R = CH_3) was destroyed under the saponification conditions was not unexpected, but the isolation of a highly crystalline water-insoluble zwitterion like **6** was very much unexpected. In one case, the dipotassium salt of the saponification product was isolated and its ^1H NMR and ^{13}C NMR spectra were determined. The C-4 and C-5 protons were present as in the oxazoline, not as they appear in the *N*-benzoyl derivative, **10**, and the C-2 carbon atom appeared as expected at 167.2 ppm (Me_2SO-d_6). Apparently the oxazoline ring *was* intact until the solution was acidified giving the fortuitously insoluble zwitterion, **6**. Under similar conditions of saponification, the oxazoline monoester **2** (R = H; R′ = CH_3) gave the corresponding oxazoline acid in excellent yield.

The exhanced reactivity of the oxazoline 2 position in **4** (R = CH_3) as compared to **2** (R = H; R′ = CH_3) can be rationalized by invoking the electron-withdrawing inductive effect of the 5-carbomethoxy group, but it would seem to be only a partial explanation for the apparent total redirection of the reaction of **4** with hydroxylamine.

Experimental Section

All melting points were taken on a Nalge-Axelrod hot stage and are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Infracord Model 257 or Model 631. The proton NMR spectra were recorded using either a Varian T-60 or HA-100 spectrometer and were calibrated by the side band modulation technique with either tetramethylsilane (Me_4Si) or 3-(trimethylsilyl-)propanesulfonic acid sodium salt as the internal standard. ^{13}C NMR spectra were recorded on a Jeol spectrometer using Me_4Si as a standard and chemical shifts were determined by computer scan. Radial paper chromatography was carried out on 31-cm Whatman No. 1 circles having a 1-cm diameter center hole. Compounds were visualized using ninhydrin (N). Thin layer chromatography was carried out on Kodak ultraviolet-sensitive silica gel sheets and was visualized in a uv lamp box.

Starting Materials. DL-*threo*-β-Hydroxyaspartic acid and DL-*erythro*-β-hydroxyaspartic acid were prepared by the method of Jones and Stammer[2] in 93% yield and benzamidoxime was prepared according to the method of Tiemann.[10]

DL-*trans*-2-Phenyl-4,5-dicarbomethoxy-2-oxazoline (4).[11] To a solution of 4.9 g (26 mmol) of ethyl benzimidate hydrochloride in 50 ml of *N*,*N*-dimethylformamide (DMF) was added 4 ml (29 mmol) of triethylamine and the solution was stirred for 10 min. A solution of 5.4 g (26 mmol) of **3** (R = CH_3) hydrochloride in 30 ml of DMF was added and the reaction mixture was stirred at room temperature for 24 hr. The resulting orange solution was concentrated in vacuo and 50 ml of water and 100 ml of ether were added. The resulting water layer was extracted with three 100-ml portions of ether and the combined ether layers were extracted with three 100-ml portions of water. After drying with anhydrous magnesium sulfate, the ether solution was percolated through a thin pad of Woelm No. 1 grade neutral alumina to remove the reddish-orange color. The resulting colorless solution was concentrated to yield 3.30 g of **4** which was recrystallized from ether–petroleum ether: 3.2 g (54%); mp 59–60°; ir (Nujol) 1750 (C=O), 1660 cm^{-1} (C=N); ^1H NMR (Me_2SO-d_6) δ 4.0 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 5.7 (d, 1 H, CHN, J = 6 Hz), 6.3 (d, 1 H, CHO, J = 6 Hz), 8.0 ppm (m, 5 H, Ph); ^{13}C NMR (off resonance, Me_2SO-d_6) 169.1 (s, C=O), 168.3 (s, C=O), 163.5 (s, C=N), 131.7–125.4 (m, phenyl), 77.6 (d, C—5), 71.7 (d, C—4), 52.4 (q, CH_3, both esters).

Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 58.89; H, 5.07; N, 5.48.

DL-*threo*-*N*-(1-Hydroxyiminobenzyl)-β-hydroxyaspartic Acid Dimethyl Ester[12] **(5).** To a solution of 262 mg (3.8 mmol) of

NH_2OH·HCl in 15 ml of absolute methanol was added 8.0 ml (3.8 mmol) of 0.48 *N* sodium methoxide and the solution was stirred for 10 min. The mixture was filtered and the filtrate was added to a solution of 1.00 g (3.8 mmol) of **4** (R = CH_3) in absolute methanol. The solution was stirred at 25° for 1 hr after which the white precipitate (239 mg) was collected. A second crop was obtained (146 mg) after allowing the filtrate to stand at 5° overnight, bringing the total yield to 385 mg of **5** (35%): mp 163–166° dec; ir (Nujol) 3448 (OH), 3390 (NH), 1754 (C=O, esters), 1645 (C=N, oxime); ^{1}H NMR (Me_2SO-d_6) δ 4.1 (s, 3 H, OCH_3), 4.13 (s, 3 H, OCH_3), 5.1 (m, 2 H, CHN and CHO), 7.8 ppm (m, 5 H, Ph); ^{13}C NMR (off resonance, Me_2SO-d_6) 170.4 (s, C=O), 169.6 (s, C=O), 152.2 (s, C=NOH), 131.1–127.1 (m, phenyl), 70.4 (d, MeO_2C–CHOH), 58.2 (d, MeO_2C–CHNH), 51.7 (q, CH_3 esters).

Anal. Calcd for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.45. Found: C, 52.81; H, 5.43; N, 9.27.

DL-*threo*-*N*-Benzoyl-β-hydroxyaspartic Acid (10). In a 250-ml round-bottom flask equipped with a stirrer and pH electrode, 1.0 g (6.7 mmol) of DL-*threo*-**3** (R = H) was placed in 14 ml of 1 *N* LiOH and the mixture was stirred mechanically until the solid dissolved. After addition of 3 ml of dimethoxyethane (DME) to the mixture, 940 mg (6.7 mmoles) of benzoyl chloride dissolved in 3 ml of DME was slowly added. The pH of the mixture was kept above 10.0 by the slow addition of 7.0 ml of 1.0 *N* LiOH and after 1 hr the solution was acidified to pH 1.8 with 1.0 *N* HCl. The acidic reaction mixture was extracted with three 50-ml portions of ethyl acetate, and the combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to a pale yellow oil which solidified within a few minutes. The white crystals were washed with ether and dried in vacuo to yield 1.60 g (95%) of crude benzoyl derivative. The product was recrystallized from water: mp 173–175°; ir (Nujol) 3380 (NH), 1760 (C=O, acid), broad 1740 (C=O, acid), 1650 cm^{-1} (C=O, amide); ^{13}C NMR (Me_2SO-d_6) (proton decoupled, Me_4Si external standard) 172.4 (C=O, acid), 170.7 (C=O, acid), 166.4 (C=O, amide), 133.6–127.2 (phenyl), 70.7 (β carbon), 55.6 ppm (α carbon); ^{1}H NMR (Me_2SO-d_6) δ 4.66 [*d*, 1 H, *J* = 3 Hz, -CH(OH)-], 5.01 (q, 1 H, *J* = 3, 8 Hz, -CHNHCOPh), 7.70 (m, 5 H, phenyl), 8.16 ppm (d, 1 H, *J* = 8 Hz, -NHCOPh).

Anal. Calcd for $C_{11}H_{11}NO_6$: C, 52.18; H, 4.38; N, 5.53. Found: C, 52.25; H, 4.40; N, 5.46.

DL-*erythro*-*N*-Benzoyl-β-hydroxyaspartic Acid. This compound was prepared by the same procedure used for **10**. DL-*erythro*-**3** (R = H) (1.12 g) afforded 1.30 g (68%) of the erythro isomer, mp 157. Recrystallization from ethyl acetate–hexane (1:1) gave an analytical sample: mp 160–161°; ir (Nujol) 3455 (OH), 3390 (NH), 1745 and 1705 (C=O, acid), and 1625 cm^{-1} (CONH); ^{1}H NMR (Me_2SO-d_6) δ 4.44 [d, 1 H, *J* = 3 Hz, -CH(OH)], 5.10 (q, 1 H, *J* = 3, 8 Hz, -CHNH), 7.73 (m, 5 H, phenyl), 8.33 ppm (d, 1 H, *J* = 8 Hz, -CONH-); ^{13}C NMR (Me_2SO-d_6, proton decoupled; Me_4Si external standard) 172.2 (COOH), 170.3 (COOH), 166.2 (-CONH-), 133.7–127.3 (phenyl), 70.9 (β carbon), 55.8 ppm (α carbon).

Anal. Calcd for $C_{11}H_{11}NO_6$: C, 52.18; H, 4.38; N, 5.53. Found: C, 52.38; H, 4.41; N, 5.61.

DL-*threo*-*O*-Benzoyl-β-hydroxyaspartic Acid (6) Monohydrate. One gram (3.8 mmol) of **4** (R = CH_3) was placed in 55 ml of DME to which 304 mg (7.6 mmol) of NaOH pellets previously dissolved in 20 ml of water was added. The solution was stirred at room temperature for 10 min and the resulting clear solution was acidified with 0.1 *N* HCl to pH 2.0. A fine white precipitate was filtered and recrystallized from water to give 900 mg (93%) of pure **12**: mp 190–191°; ir (Nujol), 3500 (NH), 3240, 3350 (OH), 1720 (C=O, acid); 1670 cm^{-1} (NH–H_2O); ^{1}H NMR (Me_2SO-d_6, Me_4Si external standard) δ 7.8 (m, 5 H, phenyl), 6.7 (m, 6 H, H_2O, NH, 2 CO_2H, OH), 5.7 (d, 1 H, HC-5, *J* = 8 Hz), 4.3 ppm (d, 1 H, HC-4, *J* = 8 Hz); ^{13}C NMR (Me_2SO-d_6, Me_4Si external standard proton decoupled) 167.8 (C=O, acid), 167.6 (C=O, acid), 164.3 (PhC=O), 133.3–128.2 (phenyl), 70.2 (COC), 52.5 ppm (CNH).

Anal. Calcd for $C_{11}H_{13}NO_7$: C, 48.71; H, 4.83; N, 5.16. Found: C, 48.78; H, 4.84; N, 5.18.

DL-*threo*-*O*-Benzoyl-β-hydroxyaspartic Acid (6). Drying 383.7 mg (1.42 mmol) of **6** monohydrate in an Abderhalden apparatus for 3 days at 82° and 0.025 Torr gave 359 mg (100%) of **6**: mp 185–187°; ir (Nujol) 3190 (NH), 3090 (OH), and 1715 cm^{-1} (COOH); ^{1}H NMR (Me_2SO-d_6) δ 4.24 (d, 1 H, *J* = 8 Hz, HC-4), 5.44 (d, 1 H, *J* = 0 Hz, HC-5), 7.7 ppm (m, 6 H, phenyl, NH).

Anal. Calcd for $C_{11}H_{11}NO_6$: C, 52.18; H, 4.38; N, 5.53. Found: C, 52.33; H, 4.42; N, 5.48.

DL-*threo*-*O*-Benzoyl-β-hydroxyaspartic Acid Hydrochloride (7). A suspension of 2.21 g (8.16 mmol) of **6** monohydrate in 13 ml of thionyl chloride was stirred magnetically for 16 hr. The suspended white solid was filtered and dried in vacuo, giving 2.24 g (94%) of **7**: mp 138–140°; ir (Nujol) 3190–3060 (broad NH_3^+), 1695 cm^{-1} (COOH); ^{1}H NMR (Me_2SO-d_6) δ 4.62 (d, 1 H, *J* = 3 Hz, -CH-), 5.80 (d, 1 H, *J* = 3 Hz, -CH-), 7.90 (m, 5 H, phenyl), 10.56 ppm (broad s, 4 H, COOH, NH_3^+); ^{13}C NMR (Me_2SO-d_6) (proton decoupled; Me_4Si external standard) 167.1 (COOH), 166.7 (COOH), 164.3 (PhCOO-) 134.0–128.0 (phenyl), 70.1 (β carbon), 52.7 (α carbon).

Anal. Calcd for $C_{11}H_{12}O_6NCl$: C, 45.61; H, 4.18; N, 4.84. Found: C, 45.57; H, 4.17; N, 4.85.

DL-*threo*-*O*-Benzoyl-β-hydroxyaspartic Acid Dimethyl Ester Hydrochloride (8). To a solution of 15 ml of acetyl chloride in 50 ml of methanol was added 1.0 g (3.47 mmol) of **7**. The solution was refluxed for 16 hr and the solvent was evaporated in vacuo, giving 0.97 g of an amorphous solid. Crystallization from isopropyl alcohol–ether gave 0.85 g (77%) of an analytical sample of **8**: mp 142–145°; ir (Nujol) 1750, sh 1740 cm^{-1} ($COOCH_3$); ^{1}H NMR (Me_2SO-d_6) δ 4.78 (d, 1 H, *J* = 4 Hz, -CH-), 5.86 (d, 1 H, *J* = 4 Hz, -CH-), 7.95 (m, 5-H, phenyl); ^{13}C NMR (Me_2SO-d_6, proton decoupled, Me_4Si external standard) 166.1 (PhCOO-), 165.7 ($COOCH_3$), 164.2 ($COOCH_3$), 134.1–127.5 (phenyl), 69.9 (β carbon), 53.4 (both CO_2CH_3) 52.6 ppm (α carbon).

Anal. Calcd for $C_{13}H_{16}NO_6Cl$: C, 49.20; H, 5.04; N, 4.41. Found: C, 49.15; H, 4.92; N, 4.55.

DL-*threo*-β-Hydroxyaspartic Acid Dimethyl Ester (9) from 8. A solution of 579 mg (1.8 mmol) of **16** and 25 ml of concentrated HCl was refluxed for 16 hr and the solvent was evaporated in vacuo. The oily product was dissolved in methanol saturated with dry HCl and after 3 hr the solvent was evaporated in vacuo and the oily residue was redissolved in methanol and evaporated in dryness in vacuo. Crystallization of the crude residue from methanol–ether gave 166 mg (43%) of **9**, mp 133–135° (lit.[10] 134–136°).

Registry No.—DL-*threo*-**3** (R = CH_3), 13515-98-5; DL-*threo*-**3** (R = H), 4294-45-5; DL-*erythro*-**3** (R = H), 6532-76-9; **4** (R = CH_3), 56454-02-5; **5**, 56454-03-6; **6**, 56454-04-7; **7**, 56454-05-8; **8**, 56454-06-9; **10**, 56454-07-0; **10** erythro isomer, 56454-08-1; ethyl benzimidate hydrochloride, 5333-86-8; NH_2OH·HCl, 5470-11-1; benzoyl chloride, 98-88-4; methanol, 67-56-1.

References and Notes

(1) C. H. Stammer, A. N. Wilson, C. F. Spencer, F. W. Bachelor, F. W. Holly, and K. Folkers, *J. Am. Chem. Soc.*, **79**, 3236 (1957).
(2) C. W. Jones, III, D. E. Leyden, and C. H. Stammer, *Can. J. Chem.*, **47**, 4363 (1969).
(3) D. F. Elliott, *J. Chem. Soc.*, 589 (1949).
(4) In the original work (ref 1), 2-phenyl-4-carbomethoxy-2-oxazoline was converted into the corresponding hydroxamic acid using NH_2OH–$NaOCH_3$ (1:1) in 80% yield.
(5) F. Feigl, "Spot Tests in Organic Analysis", American Elsevier, New York, N.Y., 1966, p 93.
(6) (a) A. Pinner, *Chem. Ber.*, **17**, 184 (1884); (b) W. Lossen, *ibid.*, **17**, 1587 (1884).
(7) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962, p 30.
(8) The β-hydroxyaspartic acids themselves have rather nondescript infrared spectra and very broad melting points, especially as hydrochlorides. Their conversions to the diesters allow easy identification.
(9) Unpublished results.
(10) F. Tiemann, *Chem. Ber.*, **17**, 126 (1884).
(11) This compound was first prepared in these laboratories by T. W. Kethley, Jr.
(12) This compound was first prepared in these laboratories by Mrs. Ann McCall.