Tetrahedron Vol. 33, pp. 881 to 883 Pergamon Press 1977 Printed in Great Britain

# SYNTHESIS OF N-SUBSTITUTED AZIRIDINE-2-CARBOXYLATES

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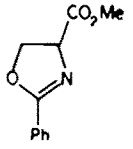
(*Received in the UK 29 March 1976; accepted for publication 14 September 1976*)

**Abstract**—The synthesis of the methyl esters of *N*-methoxycarbonyl- and *N*-benzyloxycarbonylaziridine-2-carboxylic acid **2** by reacting methyl 2-chloro-*N*-carbalkoxyglycinate **1** with diazomethane is described. The aziridines were readily converted to derivatives of *O*-methylserine **5** and *S*-methylcysteine **6**.

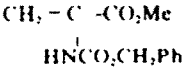
Aziridines are generally prepared by a base-catalysed elimination of hydrogen halide from β-haloamides or by a nitrene-type addition to an olefinic double bond.[1] Relatively few cases of a "carbene type" addition to a carbon–nitrogen double bond have been described in the literature.[1,2]

In the course of a study on the amidoalkylation of aromatic compounds, olefins, and active methylene compounds with glyoxylic acid derivatives,[3] we have prepared methyl 2-chloro-*N*-acylglycinates **1** and found that they will react with diazomethane at room temperature to give intermediates **4** which upon further heating in chloroform solution afforded methyl *N*-acylaziridine-2-carboxylate **2** in 30–35% yield. A plausible mechanism for the reaction is that the diazomethane functions first as a base and converts the chloro-compound **1** to the unstable acylimine **3**, which reacts with further diazomethane in a [3 + 2]-cycloaddition reaction to give the *N*-acyltriazoline derivative **4**. The latter loses nitrogen on heating to give the aziridine **2**.[1,2,4] In the case of the *N*-benzoyl derivative, there is a concomitant partial rearrangement to the oxazoline derivative.[3] The mixture of the benzoylaziridine **2a** and the 2-phenyloxazoline **7** was separated on a Florisil column. The crude reaction products do not show any of the aziridine absorptions at 3.2 and 2.5 ppm in the NMR and do not show NH absorptions in the IR. Attempts to prove the triazoline structure **4** by isolating it to the more stable triazole derivative on oxidation[5] afforded only the aziridine derivative. Addition of Pd-C to a methanol solution of the triazoline **4b** was accompanied by effervescence and the product was again the *N*-acylaziridine derivative. Solvolysis of the *N*-carbalkoxyaziridine **2** or its precursor **4** in methanol containing sulfuric acid as catalyst, afforded the esters of β-methoxy-*N*-acylalanine **5** which were identical with authentic samples prepared from commercially-available *O*-methyl-DL-serine. The two *N*-carbalkoxyaziridines were also found to react with methylmercaptan in methylene chloride and in the presence of boron trifluoride etherate to give the *S*-methyl cysteine derivatives **6**. A similar ring opening of aziridinecarboxylic acid is described in the literature.[6]

Methyl α-chlorohippurate, when treated with diazomethane, was found to give a mixture of the aziridine derivative **2a** and the 2-phenyloxazoline ester **7**. No intermediate oil was formed and there is no evidence for the presumed triazoline intermediate. From the NMR spectra we cannot rule out the 5-substituted isomer. Methyl *N*-benzyloxycarbonylaziridine - 2 - carboxylate partly decomposed on a Florisil column to give methyl *N*-benzyloxycarbonyldehydroalaninate **8**.[7,8]

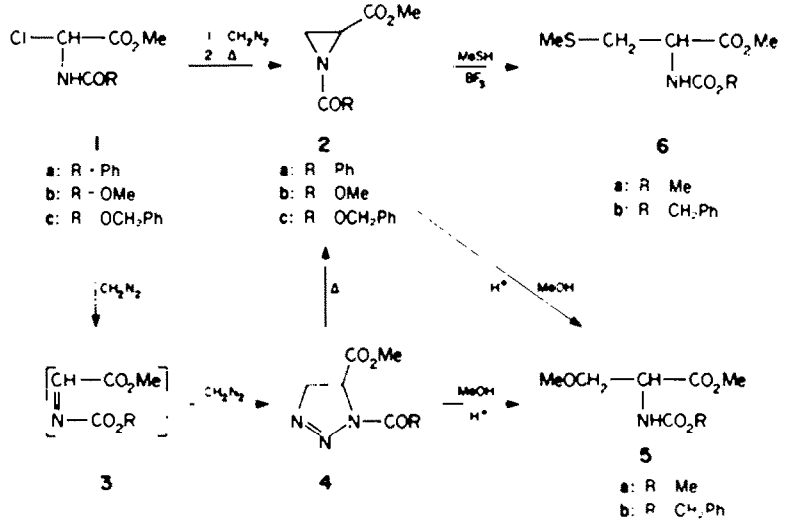


**7**

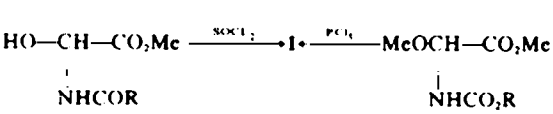


**8**

Methyl α - chloro - *N* - acylglycinate **1** used in the reactions described above were prepared from methyl α -



hydroxy - *N* - acylglycinate **9** by treatment with thionyl chloride or, in the case of the carbalkoxy derivatives, from the α - methoxy - *N* - acylglycinate and phosphorus pentachloride.



**9**

a, R=Ph
b, R=OMe
c, R=$OCH_2Ph$

**10**

a, R=Me
b, R=$CH_2Ph$

## EXPERIMENTAL

*General.* M.ps are uncorrected. The IR spectra were recorded on a Perkin-Elmer 237 spectrometer; NMR spectra were obtained on a Varian T-60 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Mass spectra were recorded on Atlas CH4MAT mass spectrometer.

*Methyl glyoxylate hemiacetal.*[9] A solution of glyoxylic acid monohydrate (23.0 g, 0.25 mole) in methanol (125 ml) was refluxed overnight. The solution was cooled to room temp. and neutralized with solid $KHCO_3$ (a very small amount was required). The neutral solution was evaporated *in vacuo* and the oily residue was dissolved in $CH_2Cl_2$ and dried with $Na_2SO_4$. Evaporation afforded the methyl glyoxylate hemiacetal in 82% yield. IR($CHCl_3$): 3630, 2840, 1750 and 1700 cm$^{-1}$; NMR ($CDCl_3$)δ: 3.49 (s, 3H), 4.96 (s, 1H broad), 5.40 (s, 1H). The crude oily product was used in the following reactions without further purification.

*Methyl α-hydroxyhippurate* (**9a**). A suspension of methyl glyoxylate hemiacetal (6.60 g, 0.055 mole) and benzamide (6.05 g, 0.05 mole) in benzene (50 ml) was refluxed overnight. The solution was concentrated (25 ml) and left at room temp. The crystalline material which separated was filtered and dried; yield 7.55 g. (72.3%); m.p. 108–109°. IR ($CHCl_3$): 3550, 3430, 1750, 1665 and 1585 cm$^{-1}$; NMR ($CDCl_3$)δ: 8.07–7.42 (m, 6H), 5.94 (d, 1H, J = 8), 4.87 (s, 1H), 3.86 (s, 3H); MS: m/e 209 (Found: C, 57.70; H, 5.35; N, 7.02. $C_{10}H_{11}NO_4$ requires: C, 57.41; H, 5.30; N, 6.70%).

*Methyl N - methoxycarbonyl - α - hydroxyglycinate* (**9b**). A solution of methyl glyoxylate hemiacetal (6.6 g, 0.055 mole) and methyl carbamate (3.75 g., 0.05 mole) in benzene (50 ml) was refluxed overnight. The solution was concentrated to a small volume (10 ml) and petroleum ether (100 ml, 40–60°) was added. The mixture was magnetically stirred overnight until a nicely dispersed solid was obtained. The solid which melted at 93–95° (87%) was filtered and dried. IR ($CHCl_3$): 3550, 3420, 2850, 1725 and 1500 cm$^{-1}$; NMR ($CDCl_3$)δ: 6.51 (d, 1H, J = 9), 5.60 (d, 1H, J = 9); 4.86 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H). MS: m/e: 162 (Found: C, 36.94; H, 5.53; N, 8.51. $C_4H_7NO_5$ requires: C, 36.81; H, 5.56; N, 8.59%).

*Methyl N - methoxycarbonyl - α - methoxyglycinate* (**10a**). To an ice-cooled, stirred, solution of *N* - methoxycarbonyl - α - hydroxyglycine[9] (11.2 g, 0.075 mole) in abs MeOH (150 ml) there was added conc. sulfuric acid (2 ml, 96%). The solution was left at room temp. for 48 h, poured into ice- and saturated $NaHCO_3$ and the organic material was extracted 3 times with EtOAc. Drying ($MgSO_4$), filtering and evaporation of the solvent left an oil which was purified on a deactivated neutral alumina (120 g + 12 ml MeOH) column. Elution with benzene gave 8.0 g (60.2%) cyrstalline product. IR ($CHCl_3$): 3420, 2830, 1745–1725 and 1510 cm$^{-1}$; NMR ($CDCl_3$)δ: 3.49 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 5.40 (d, 1H, J = 10) and 6.15 (d, 1H, J = 10, broad); MS: m/e 177; (Found: C, 40.28; H, 6.20; N, 7.83. $C_5H_{11}NO_5$ requires: C, 40.68, H, 6.26; N, 7.91%).

*Methyl N - benzyloxycarbonyl - α - hydroxyglycinate* (**9c**). A solution of methyl glyoxylate hemiacetal (2.64 g, 0.022 mole) and benzyl carbamate (3.02 g, 0.02 mole) in benzene (50 ml) was refluxed overnight. The solvent was evaporated under reduced pressure and the residue was triturated with ether-light petroleum ether (50 ml + 50 ml) and filtered to give 2.4 g (50.2%) of product; m.p. 92–93°; IR ($CHCl_3$): 3540, 3430, 1750–1720, and 1510 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.42 (s, 5H), 6.11 (d, 1H, broad), 5.55 (d, 1H, J = 9, 5.19 (s, 2H) and 3.84 (s, 3H); MS: *m/e* 239.1; (Found: C, 55.33; H, 5.56; N, 5.93. $C_{11}H_{13}NO_5$ requires: C, 55.23; H, 5.48; N, 5.86%).

*Methyl N - methoxycarbonyl - α - chloroglycinate* (**10b**. To a suspension of methyl *N* - methoxycarbonyl - α - hydroxyglycinate (0.344 g, 0.002 mole) in $CH_2Cl_2$ (ethanol-free) there was added thionyl chloride (0.29 ml, 0.04 mole). The suspension was refluxed for 1 h and the resulting clear solution was concentrated *in vacuo*. The oily residue was triturated with light petroleum to give a white crystalline solid; m.p. 43–44° (79%). IR ($CHCl_3$): 3410, 2850, 1730 and 1510 cm$^{-1}$; NMR ($CDCl_3$) δ: 3.79 (s, 3H), 3.87 (s, 3H), 6.26 (s, broad, 2H). (Found: C, 32.80; H, 4.77; N, 7.60. $C_4H_6NO_4Cl$ requires: C, 34.04; H, 4.45; N, 7.72; Cl, 19.54%).

*Methyl N - benzyloxycarbonyl - α - chloroglycinate* (**1c**. To a suspension of methyl - *N* - benzyloxycarbonyl - α - methoxyglycinate (6.31 g, 0.025 mole) in dry $CCl_4$ (125 ml) there was added phosphorus pentachloride (8.3 g). The reaction mixture was stirred at room temp. until the $PCl_5$ disappeared (48 h). The reaction was also followed by NMR (disappearance of the methoxy group). The solution was concentrated *in vacuo* and the solid residue was triturated overnight with dry light petroleum and filtered through a sinter glass to give 5.31 g. (82.5%) of a white solid; m.p. 69–70°. IR($CHCl_3$): 3410, 1770 and 1505 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.43 (s, 5H), 6.26 (s, 2H, broad), 5.23 (s, 2H), 3.88 (s, 3H), (Found: C, 51.36; H, 4.85; N, 5.50; Cl, 13.47. $C_{11}H_{12}NO_4Cl$ requires: C, 51.30: H, 4.70 N, 5.44; Cl, 13.77%). The same chloride was also obtained from methyl - *N* - benzyloxycarbonyl - α - hydroxyglycinate and $SOCl_2$ in $CH_2Cl_2$ as described above for the preparation of the methoxycarbonyl derivative.

*Reaction of methyl - α - chlorohippurate with diazomethane* (**2a**. A solution of the chloro compound (3.135 g, 0.015 mole) in $CH_2Cl_2$ (15 ml) was added dropwise to an excess (3 eq) of $CH_2N_2$ in ether (0°). After 48 h at room temperature the solution was filtered, washed with aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated. The oily residue (2.42 g) was chromatographed over Florisil (120 g). The column was eluted with $CH_2Cl_2$:$CHCl_3$ (1 : 1) mixture to give methyl *N* - benzoylaziridine - 2 - carboxylate (0.326 g, 14.5%); IR ($CHCl_3$): 1740, 1680, 1600, 1440, 1320 and 1295 cm$^{-1}$; NMR ($CDCl_3$)δ: 8.30–7.32 (m, 5H, Ph), 3.68 (s, 3H, $CH_3OCO$), 3.29 (q, 1H, J = 5.5, CH), 2.89–2.60 (m, 2H, $CH_2$). (Found: C, 63.97; H, 5.42; N, 6.73. $C_{11}H_{11}NO_3$ requires: C, 64.38; H, 5.40; N, 6.83%); b.p. 120° (0.6 mm); MS(HR) for $C_{11}H_{11}NO_3$: *m/e* 205.0710 (required: 205.0738).

The aziridine derivative was followed by methyl 2 - phenyloxazoline - 4 - carboxylate which was eluted with $CHCl_3$ (0.42 g, 5.0%). IR ($CHCl_3$): 1735, 1655, 1640, 1580, 1485, 1450, 1440, 1365 and 1260 cm$^{-1}$; NMR ($CDCl_3$)δ: 8.3–7.4 (m, 5H, Ph), 5.24–4.19 (m, 3H, $CH_2CH$), 3.87 (s, 3H, $CH_3OCO$) (Found: C, 64.13; H, 5.51; N, 6.64. $C_{11}H_{11}NO_3$ requires: C, 64.38; H, 5.40; N, 6.83%); b.p. 110° (0.5 mm); MS (HR): *m/e* 205.0762; $C_{11}H_{11}NO_3$ requires: 205.0739.

*Reaction of methyl N - methoxycarboxyl - α - chloroglycinate with diazomethane.* A solution of the chloro compound **1b** (4.90 g, 0.03 mole) dissolved in $CH_2Cl_2$ (25 ml) was added dropwise to a cooled (0°) ethereal solution (3 eq in 150 ml) of diazomethane. The reaction solution was left at room temp. for 1 h and was divided into two 85 ml portions: *Procedure A*. The first portion was filtered and carefully evaporated in vacuo (30°), to give a yellow oil (2.4 g, 89%). The oil did not show any aziridine absorptions in the NMR (2.5 and 3.2 ppm). IR ($CHCl_3$): 3040, 2960, 1735, 1500, 1450, 1390, 1345, 1290, 1200, 1160, 1013 and 920 cm$^{-1}$; NMR ($CDCl_3$)δ: 4.66 (s + q, 2H), 3.96 (s, 3H), 3.81 (s, 3H). The triazoline was slowly converted, in the NMR tube, to the aziridine derivative. The crude oil was dissolved in chloroform, the solution refluxed for 2 h and evaporated again to give an oil which showed 39.5% aziridine according to NMR. The product was chromatographed on a Florisil column (70 g) and eluted with $CH_2Cl_2$ to give 0.80 g (33.6%) of pure methyl *N* - methoxycarbonylaziridine - 2 - carboxylate. IR ($CHCl_3$): 2990, 2955, 2850, 1735, 1440, 1385, 1330, 1305 and 1180 cm$^{-1}$; NMR ($CDCl_3$)δ: 3.80 (s, 3H, $CH_3OCO$), 3.77 (s, 3H, $CH_3OCON$), 3.12 (q, 1H, J = 5.5, CH), 2.67–2.40 (m, 2H, $CH_2$); MS (HR): *m/e* 159.0521; $C_6H_9NO_4$ requires: 159.0446. (Found: C, 45.35; H, 5.74; N, 8.64. $C_6H_9NO_4$ requires: C, 45.28; H, 5.70; N, 8.80%).

*Procedure B.* To the second portion was added $NaHCO_3$ (35 ml of a saturated solution) and the mixture was stirred for 1 h, the organic layer was separated, dried ($MgSO_4$), and evaporated. The oily residue (1.087 g, 45.5%) is according to the NMR 79.0% aziridine derivative. It was purified as described above.

*Reaction of methyl N - benzyloxycarbonyl - α - chloroglycinate with diazomethane.* To a cooled (0°) freshly prepared ethereal solution of diazomethane (3 eq) there was added methyl *N* - benzyloxycarbonyl - α - chloroglycinate (6.5 g, 0.0254 mole) dissolved in $CH_2Cl_2$ (20 ml). After 0.5 h at room temp. there was added aqueous saturated $NaHCO_3$ (50 ml) and ether (50 ml). The mixture was stirred for 0.5 h, the organic layers were separated, dried ($MgSO_4$) and evaporated. The crude oily product (3.0 g), which did not show any aziridine absorptions in the NMR at δ 2.5 and 3.2, was dissolved in $CHCl_3$ (25 ml) and the solution was refluxed for 3 h, evaporated and chromatographed over silica gel (150 g). The pure aziridine was eluted with $CH_2Cl_2$ (1.96 g, 33%). IR ($CHCl_3$): 1730, 1595, 1435, 1375, 1320 and 1170 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.41 (s, 5H); 5.10 (s, 2H), 3.72 (s, 3H); 3.12 (d of d, 1H, J = 5.5); 2.67–2.37 (m, 2H); MS: *m/e* 235.1. (Found: C, 61.17; H, 5.57; N, 6.03. $C_{12}H_{13}NO_4$ requires: C, 61.21; H, 5.57; N, 5.96%).

*Methyl N - benzyloxycarbonyldehydroalaninate*[9] **8.** This compound was isolated in various amounts during the purification of the *N* - benzyloxycarbonylaziridine **2c**. According to the NMR spectrum the crude product did not contain any dehydroalanine derivative. On a Florisil column as much as 24% of the aziridine was converted to the dehydro derivative. On a silica column only traces of the latter compound was obtained. MS (HR): *m/e* 235.0819, $C_{12}H_{13}NO_4$ requires: 235.0844; IR ($CHCl_3$): 3490, 1720, 1700, 1620, 1515; NMR ($CDCl_3$)δ: 7.45 (s, 6H, Ph + NH), 6.30 (s, 1H), 5.81 (d, 1H, J = 1), 5.20 (s, 2H, $OCH_2$), 3.87 (s, 3H).

*Methyl N - methoxycarbonyl - O - methyl - DL - serinate* **5a.** To a cooled methanolic (10 ml) solution of methyl *N* - methoxycarbonylaziridine - 2 - carboxylate (0.40 g) there was added conc. $H_2SO_4$ (0.25 ml, 96%). After 24 h at room temp. the acid was neutralized with solid $KHCO_3$, the solution filtered and evaporated in vacuo. The oily product was dissolved in ether (50 ml), decanted from undissolved residue and evaporated again (0.33 g, 68%). The methyl ester was identical through IR, NMR and MS with an authentic sample prepared from *O* - methyl - DL - serine as described below. The methyl ester **5a** was further hydrolyzed (KOH, aq. MeOH) to the corresponding acid which was identical with an authentic sample (m.m.p., IR and NMR) prepared from *O* - methyl - DL - serine as described below.

*Methyl N - benzyloxycarbonyl - O - methyl - DL - serinate* **5b.** Methyl - α - chloro - *N* - benzyloxycarbonylglycinate (0.01 mole) was treated with diazomethane as described above. The crude $CH_2Cl_2$ solution containing the triazoline was diluted with methanol (40 ml) and concentrated sulfuric acid (1 ml, 96%) was added. After 45 min at 0°C the solution was left overnight at room temp. The reaction mixture was neutralized with solid $KHCO_3$, evaporated and extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to give 1.27 g (47.7%) of oil. The crude ester was identical (IR and NMR) with an authentic sample described below. No attempts were made to purify the ester, it was hydrolyzed to the *N* - *benzyloxycarbonyl* - *O* - methyl - DL - serine in methanolic KOH. The acid was crystallized from ethylacetate-hexane, m.p. 71–72°; MS: *m/e* 253.1; IR ($CHCl_3$): 3430, 1715 and 1510 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.36 (s, 5H, Ph), 5.81 (d, 1H, J = 7, NH), 5.15 (s, 2H, $OCH_2$ Ph), 4.73–4.37 (m, 1H, CH), 3.94 (m, 2H, $OCH_2$) and 3.33 (s, 3H, $CH_3O$). The acid was identical with an authentic sample which was prepared from *O* - methyl - DL - serine and carbobenzoxy chloride as described below.

*Methyl N - methoxycarbonyl - S - methyl - DL - cysteinate* **6a.** To a cooled solution of 2b (0.8 g) in $CH_2Cl_2$ (10 ml) there was added with stirring a solution of methyl mercaptan (4.0 g, 8 eq) in $CH_2Cl_2$ (20 ml) followed by $BF_3$ etherate (1 ml). After 48 h at room temp. the $CH_2Cl_2$ solution was poured into crushed ice and saturated $NaHCO_3$. The aqueous layer was extracted with 3 × 50 ml $CH_2Cl_2$ and the combined $CH_2Cl_2$ solution was dried ($MgSO_4$) and evaporated. The oily residue (0.5 g, 48%) showed IR ($CHCl_3$) absorptions at 3430, 2850, 1720 and 1500 cm$^{-1}$; NMR ($CDCl_3$)δ: 5.84 (s, 1H, NH), 4.55 (s, 1H, CH), 3.78 (s, 3H, $CH_3OCO$), 3.6 (s, 3H, $CH_3OCON$), 2.95 (d, 2H, J = 5.5, $S-CH_2$) and 2.12 (s, 3H, $CH_3S$). The ester was hydrolysed (KOH, aq MeOH) to the acid, IR ($CHCl_3$): 3520, 3430, 1720 and 1505 cm$^{-1}$; NMR ($CDCl_3$)δ: 9.89 (s, 1H, COOH), 5.94 (sh, 1H, NH), 4.87–4.34 (m, 1H, CH), 3.71 (s, 3H, $CH_3OCON$), 3.05, 2.98 (s + d, 2H, J = 2.5, $CH_2S$), 2.14 (s, 3H, $CH_3S$) MS (HR): *m/e* 193.0408; $C_6H_{11}NO_4S$ requires: 193.0410.

*Methyl N - benzyloxycarbonyl - S - methyl - DL - cysteinate.* To a cooled (0°) solution of methyl *N* - benzyloxyaziridine - α - carboxylate (0.46 g, 0.002 mole) in $CH_2Cl_2$ there was added MeSH (2 g, excess) in $CH_2Cl_2$ (10 ml) and $BF_3$ etherate (0.4 ml). After 24 h at room temp. the solution was evaporated, the residue was redissolved in $CH_2Cl_2$ (60 ml) washed with aqueous $NaHCO_3$ (10 ml), dried ($MgSO_4$) and evaporated again. The oily residue (0.44 g, 79.5%) showed: IR ($CHCl_3$): 3420, 1750, 1720 and 1510 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.44 (s, 5H, Ph), 5.75 (d, broad, 1H, NH), 5.2 (s, 2H, $OCH_2$), 4.83–4.51 (m, 1H, CH), 3.80 (s, 3H, $CH_3OCO$), 2.79 (d, J = 5.5, 2H, $S-CH_2-$), 2.1 (s, 3H $CH_3S$); MS (HR): *m/e* 283.0871; $C_{13}H_{17}NO_4S$ requires: 283.0878. (Found: C, 55.20; H, 6.11; N, 4.95; S, 11.19. $C_{13}H_{17}NO_4S$ requires: C, 55.12; H, 6.05; N, 4.95; S, 11.29%).

*N - Benzyloxycarbonyl - O - methyl - DL - serine (authentic sample). O* - Methyl - DL - serine (1 g) was carbobenzoxylated with carbobenzoxy chloride (1.7 ml) in aq $NaHCO_3$ following the procedure described for the carbobenzoxylation of serine.[10] The acid melted at 70.5–71.5° after recrystallization from EtOAc-hexane, IR ($CHCl_3$): 3580, 3510, 3440, 2830, 1720 and 1505 cm$^{-1}$; NMR ($CDCl_3$)δ: 3.37 (s, 3H) 3.77 (o, 2H), 4.56 (m, 1H), 5.89 (d, 1H), 7.41 (s, 5H), 11.0 (s, 1H); MS: *m/e* 253. (Found: C, 56.68, H, 5.82; N, 5.73. $C_{12}H_{15}NO_5$ requires: C, 56.91, H, 5.97; N, 5.53%)

*Methyl N - benzyloxycarbonyl - O - methyl - DL - serine (authentic sample).* To a methanol solution of *N* - benzyloxycarbonyl - *O* - methyl - DL - serine (0.75 g) there was added an ethereal solution of diazomethane until the yellow color persisted. The solution was evaporated in vacuo to give an oily product 0.73 g (93%). IR ($CHCl_3$): 3439, 2840, 1750–1720 and 1505 cm$^{-1}$; NMR ($CDCl_3$)δ: 7.40 (s, 5H), 5.71 (d, 1H, J = 8), 5.16 (s, 2H), 4.59, 4.33 (2t, 1H, J = 3), 3.76 (s, 3H), 3.7 (oc., 2H), 3.33 (s, 3H); MS: *m/e* 267.

*N - Methoxycarbonyl - O - methyl - DL - serine (authentic sample).* To a solution of *O* - methyl - DL - serine (0.5 g) in saturated aqueous $NaHCO_3$ (18 ml) there was added, with stirring and cooling, methyl chloroformate (1 ml). After 3 h at room temp. the solution was acidified with conc. HCl and extracted with 3 × 25 ml of EtOAc. The EtOAc solution was dried ($MgSO_4$) and evaporated. The oily residue (0.74 g, 97%) was triturated with light petroleum to give the crystalline acid which was crystallized from EtOAc-light petroleum, m.p. 72.5°, IR ($CHCl_3$): 3520, 3430, 2830, EtOAc-light petroleum, m.p. 72.5°, IR ($CHCl_3$): 3520, 3430, 2830, 1715 and 1500 cm$^{-1}$; NMR ($CDCl_3$)δ: 10.45 (s, 1H), 5.86 (d, 1H, J = 8 cps), 4.74–4.33 (sex., 1H), 3.78 (oc., 2H), 3.75 (s, 3H) and 3.40 (s, 3H); MS (HR): *m/e* 177.0628; $C_6H_{11}NO_5$ requires: 177.0537 (Found: C, 40.74, H, 6.60, N, 7.80. $C_6H_{11}NO_5$ requires: C, 40.68, H, 6.26; N, 7.91%). The acid was converted with diazomethane in ether solution to the oily methyl ester. IR ($CHCl_3$): 3435, 2840, 1750, 1720 and 1500 cm$^{-1}$; NMR ($CDCl_3$)δ: 5.64 (d, broad, 1H), 4.56, 4.42 (2t, 1H, J = 3.5), 4.0–3.47 (oc, 2H) 3.78 (s, 3H), 3.72 (s, 3H), 3.35 (s, 3H). MS (HR): *m/e* 191.0815; $C_7H_{13}NO_5$ requires: 191.0793.

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