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Boron Analogues of Amino Acids. 4.[1] Synthesis of Glycine and N-Methylated Glycine Ester Analogues

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Selected representatives of a series of esters derived from boron analogues of amino acids and having the general formulation amine·BH_2COOR (amine = $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3; R = CH_3, CH_2CH_3, CH_2CH_2Cl) were prepared in good to excellent yields by condensing the corresponding acids and alcohols with dicyclohexylcarbodiimide (DCC) at room temperature in CH_2Cl_2. $(CH_3)_2NH{\cdot}BH_2COOCH_3$ and $H_3N{\cdot}BH_2COOCH_3$ were prepared in 67% and 49% yields, respectively, by amine-exchange reactions of $(CH_3)_3N{\cdot}BH_2COOCH_3$ with $(CH_3)_2NH$ and NH_3. $(CH_3)_3N{\cdot}BH_2COOSi(CH_3)_3$ was obtained by reacting $(CH_3)_3N{\cdot}BH_2COOLi$ and $(CH_3)_3SiCl$.

Introduction

Isoelectronic and isosteric boron analogues of the amino acids glycine and betaine ($H_3N{\cdot}BH_2COOH$[2] and $(CH_3)_3N{\cdot}BH_2COOH$,[3] respectively) and their derivatives and precursors have been shown to possess interesting biological activities, in particular, significant antitumor, antiarthritic, and hypolipidemic activities in rodents.[4-6] For example, $(CH_3)_3N{\cdot}BH_2COOH$ afforded 82% inhibition of tumor growth in the Ehrlich Ascites screen[4] and lowered serum cholesterol levels by 49% at low dosages.[6] An ester, trimethylamine–carbethoxyborane, $(CH_3)_3N{\cdot}BH_2COOC_2H_5$ (**1**), produced 74% inhibition of the induced arthritic state[5] and lowered serum cholesterol levels[6] by 36% in animal model studies. In view of their potential biological activities, we have therefore prepared selected representative members of a series of alkyl esters having the general formulation amine·BH_2COOR (amine = $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3; R = CH_3, CH_2CH_3, CH_2CH_2Cl, $Si(CH_3)_3$) for structure–activity relationship studies. These compounds may also prove to be useful in boron neutron capture therapy for the treatment of cancer.[7]

Results and Discussion

Trimethylamine–carbethoxyborane, $(CH_3)_3N{\cdot}BH_2COOC_2H_5$ (**1**), was prepared as described previously[5] by refluxing a solution of $(CH_3)_3N{\cdot}BH_2CN$[8] in CH_2Cl_2 with 2 equiv of $(C_2H_5)_3OBF_4$[9] under dry N_2 for 24 h. The resulting *N*-

$$(CH_3)_3N{\cdot}BH_2CN \xrightarrow[CH_2Cl_2]{(C_2H_5)_3OBF_4}$$

$$(CH_3)_3N{\cdot}BH_2C{\equiv}NC_2H_5{}^+BF_4{}^- \xrightarrow[C_2H_5OH]{H^+} (CH_3)_3N{\cdot}BH_2COOC_2H_5$$

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ethylnitrilium salt (not isolated) was alcoholized at reflux temperature for 48 h with 95% ethanol and concentrated HCl. After neutralization, workup resulted in a yellow liquid, which was either crystallized or sublimed to give a 34% yield of the ethyl ester. This ester (**1**) was also made by an alternative method in 45% yield by dehydrating a solution of $(CH_3)_3N{\cdot}BH_2COOH$[3] and absolute ethanol with dicyclohexylcarbodiimide (DCC) at room temperature for 6 days. The relatively high volatility and solubility in water of this sweet-smelling ester probably contributed to its low yield by either of these procedures.

Trimethylamine–carbomethoxyborane, $(CH_3)_3N{\cdot}BH_2COOCH_3$ (**2**), was prepared in 82% yield by condensing $(CH_3)_3N{\cdot}BH_2COOH$ and CH_3OH with DCC at room temperature for 1 week; extension of the reaction period to 2 weeks led to an increase in the yield of **2** to 98%.

$$(CH_3)_3N{\cdot}BH_2COOH + CH_3OH \xrightarrow[CH_2Cl_2]{DCC} (CH_3)_3N{\cdot}BH_2COOCH_3 + (C_6H_{11}NH)_2CO$$

2 DCU

Dimethylamine–carbomethoxyborane, $(CH_3)_2NH{\cdot}BH_2COOCH_3$ (**3**), was prepared in 67% yield by an amine-exchange reaction of $(CH_3)_3N{\cdot}BH_2COOCH_3$ (**2**) with an 8-fold excess

$$(CH_3)_3N{\cdot}BH_2COOCH_3 + (CH_3)_2NH \rightarrow (CH_3)_2NH{\cdot}BH_2COOCH_3 + (CH_3)_3N$$

2 **3**

(by weight) of $(CH_3)_2NH$ in a glass pressure reaction vessel for 2 weeks at room temperature. Ca. 8% unreacted **2** in the product mixture was readily removed by washing with H_2O and vacuum pumping. The ester linkages in the starting material and product were not cleaved by the excess amine. The amine-exchange process is the preferred route as the alternative preparation of **3** by condensation of $(CH_3)_2NH{\cdot}BH_2COOH$ and CH_3OH with DCC at room temperature for 4 days gave only a very low yield (8%).

Methylamine–carbomethoxyborane, $CH_3NH_2{\cdot}BH_2COOCH_3$ (**4**), was prepared in 21% yield of condensing $CH_3NH_2{\cdot}BH_2COOH$ and CH_3OH with DCC at room temperature for 6 days.

$$CH_3NH_2{\cdot}BH_2COOH + CH_3OH \xrightarrow{DCC} CH_3NH_2{\cdot}BH_2COOCH_3 + DCU$$

4

Trimethylamine–(carbo-2-chloroethoxy)borane, $(CH_3)_3N{\cdot}BH_2COOCH_2CH_2Cl$ (**5**), was prepared in 61% yield in a manner similar to the preparation of **4** by condensing $(CH_3)_3N{\cdot}BH_2COOH$ and $HOCH_2CH_2Cl$ with DCC at room temperature for 1 week.

$$(CH_3)_3N{\cdot}BH_2COOH + HOCH_2CH_2Cl \xrightarrow{DCC} (CH_3)_3N{\cdot}BH_2COOCH_2CH_2Cl + DCU$$

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Table I. Physical and Spectral Data for Esters of Boron Analogues of Amino Acids

compd	ester	bp/mp, °C	yield, %	^{11}B chem shifts, ppm[a]	J_{B-H}, Hz
1	$(CH_3)_3N{\cdot}BH_2COOC_2H_5$	45–47	34–41	−9.17 (t)	98
2	$(CH_3)_3N{\cdot}BH_2COOCH_3$	90–92	82–98	−9.09 (t)	99
3	$(CH_3)_2NH{\cdot}BH_2COOCH_3$	52–53	67	−12.57 (t)	95
4	$CH_3NH_2{\cdot}BH_2COOCH_3$	56–57	21	−16.22 (t)	98
5	$(CH_3)_3N{\cdot}BH_2COOCH_2CH_2Cl$	...	61	−8.75 (t)	97
6	$H_3N{\cdot}BH_2COOCH_3$	92–93	49	−20.45 (t)	94
7	$(CH_3)_3N{\cdot}BH_2COOSi(CH_3)_3$	60 (0.2 torr)	58		

[a] $(C_2H_5)_2O{\cdot}BF_3$ was used as an external standard; all chemical shifts reported here were (negative) upfield from the standard.

Ammonia–carboxmethoxyborane, $H_3N{\cdot}BH_2COOCH_3$ (**6**), was prepared in 49% yield by an amine-exchange reaction[10] involving $(CH_3)_3N{\cdot}BH_2COOCH_3$ (**2**) and excess liquid NH_3 at room temperature for 2 weeks.

$$\underset{\mathbf{2}}{(CH_3)_3N{\cdot}BH_2COOCH_3} + NH_3(l) \rightarrow \underset{\mathbf{6}}{H_3N{\cdot}BH_2COOCH_3} + (CH_3)_3N$$

Trimethylamine–(carbotrimethylsiloxy)borane, $(CH_3)_3N{\cdot}BH_2COOSi(CH_3)_3$ (**7**), was prepared by a different procedure involving lithiation of $(CH_3)_3N{\cdot}BH_2COOH$ with *n*-C_4H_9Li under dry N_2 in ether and subsequent reaction of the lithium salt (not isolated) with $(CH_3)_3SiCl$ at ambient temperature for ca. 16 h. Workup and vacuum distillation afforded 58% of the silyl ester **7** as a clear, moisture-sensitive liquid that solidified on standing.

$$(CH_3)_3N{\cdot}BH_2COOH \xrightarrow{n\text{-}C_4H_9Li} (CH_3)_3N{\cdot}BH_2COOLi \xrightarrow{(CH_3)_3SiCl} \underset{\mathbf{7}}{(CH_3)_3N{\cdot}BH_2COOSi(CH_3)_3}$$

All of the new compounds were characterized by elemental analysis and IR, ^{1}H NMR and ^{11}B NMR spectroscopy. Physical and spectral data of the esters are given in Table I. IR spectra exhibited characteristic B—H and C=O absorptions; ^{1}H and ^{11}B NMR spectral data were consistent with the structures shown for the compounds.

Studies on the biological activities of these esters are in progress and will be reported elsewhere.

Experimental Section

General Data. IR spectra were recorded on a Perkin-Elmer 297 spectrometer. Solid samples were prepared as KBr disks, as Nujol mulls between NaCl disks, or as solutions in suitable solvents; oils were recorded neat. Proton and boron NMR spectra were obtained on Varian EM 360A and JEOL FX 90Q spectrometers, respectively. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY. The following compounds were purchased and used without further purification: $(CH_3)_3N{\cdot}HCl$ (Aldrich), $ClCH_2CH_2OH$ (Aldrich), $NaBH_3CN$ (Aldrich), $(CH_3)_2NH$ (Eastman), CH_3NH_2 (Union Carbide), *N,N'*-dicyclohexylcarbodiimide (Chemalog), *n*-C_4H_9Li (Alfa). $(CH_3)_3N{\cdot}BH_2CN$ was prepared[8] from $(CH_3)_3N{\cdot}HCl$ and $NaBH_3CN$. $(CH_3)_3N{\cdot}BH_2COOH$ was prepared[3] from $(CH_3)_3N{\cdot}BH_2CN$ and $(C_2H_5)_3OBF_4$[9] followed by hydrolysis. $(CH_3)_2NH{\cdot}BH_2COOH$ and $CH_3NH_2{\cdot}BH_2COOH$ were prepared[7] from $(CH_3)_3N{\cdot}BH_2COOH$ by amine-exchange reactions with $(CH_3)_2NH$ and CH_3NH_2, respectively, in 250 mL glass pressure reaction vessels that were purchased along with their safety shields from Lab-Crest Scientific Co., Warminster, PA. $(CH_3)_3SiCl$ (Aldrich) was distilled prior to use. $(C_2H_5)_3OBF_4$ was either purchased (Aldrich) or prepared by a known method.[9]

Preparation of $(CH_3)_3N{\cdot}BH_2COOC_2H_5$ (1). Method a. A solution of $(CH_3)_3N{\cdot}BH_2COOH$ (15.00 g, 0.128 mol) and DCC (29.12 g, 0.141 mol, 10% excess) in absolute ethyl alcohol (100 mL) was stirred at ambient temperature for 6 days. The solution became cloudy, and the insoluble *N,N'*-dicyclohexylurea (DCU) that formed was filtered off. Water (100 mL) was added to the filtrate, and the resulting solution was extracted with CH_2Cl_2 (4 × 100 mL). The CH_2Cl_2 extracts were treated with charcoal, dried over $MgSO_4$, and filtered. The filtrate was concentrated in a rotary evaporator, and the resulting oily material was vacuum sublimed at 50 °C. Finally, the product was crystallized from CH_2Cl_2/pentane (2:1) to give sweet-smelling crystalline **1** (7.5 g, 40.4%); the physical and chemical properties of the compound perfectly matched those reported for method b.

Method b.[5] A solution of the *N*-ethylnitrilium salt, $(CH_3)_3N{\cdot}BH_2C{\equiv}NC_2H_5{}^+BF_4{}^-$, was prepared by refluxing a mixture of $(CH_3)_3N{\cdot}BH_2CN$ (19.56 g, 0.2 mol) and 1 N $(C_2H_5)_3OBF_4$ in CH_2Cl_2 (400 mL, 0.4 mol, 100% excess) for 24 h. Following the addition of 95% C_2H_5OH (200 mL) and concentrated HCl (8 mL), the mixture was refluxed for 48 h, then cooled, and neutralized with a saturated $NaHCO_3$ solution, and the excess C_2H_5OH was removed under reduced pressure. The product was extracted from the aqueous solution with CH_2Cl_2. Drying the organic portion over $MgSO_4$ followed by solvent removal produced a yellow liquid. Purification by crystallization from diethyl ether or by sublimation afforded the sweet-smelling volatile ester **1** as a white crystalline solid (9.9 g, 34%): mp 45–47 °C; IR ($CDCl_3$) 2380 (ν_{BH}), 1660 (ν_{CO}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, CH_3), 2.76 (s, $(CH_3)_3N$), 4.07 (q, CH_2); ^{11}B NMR ($CDCl_3$, $(C_2H_5)_2O{\cdot}BF_3$) δ −9.17 (t, J_{B-H} = 98 Hz). Anal. Calcd for $C_6H_{16}BNO_2$: C, 49.70; H, 11.12; B, 7.46; N, 9.77. Found: C, 49.96; H, 11.04, B, 7.56; N, 9.56.

Preparation of $(CH_3)_3N{\cdot}BH_2COOCH_3$ (2). A solution of $(CH_3)_3N{\cdot}BH_2COOH$ (9.36 g, 0.08 mol) and DCC (25 g, 0.12 mol, 50% excess) in anhydrous CH_3OH (150 mL) was stirred at ambient temperature for 1 week. The initially clear solution turned cloudy, and DCU was precipitated gradually. Following the addition of H_2O, the mixture was extracted repeatedly with CH_2Cl_2 (5 × 100 mL). The organic portion was dried over $MgSO_4$, and the solvent was removed by rotary evaporation to give white needles of ester **2** along with some DCU as impurity. The crude product was dissolved in CH_2Cl_2, the insoluble DCU filtered off, and the solvent removed. Recrystallization of the ester from diethyl ether/pentane gave white needles (8.58 g, 82%): mp 90–92 °C; IR ($CDCl_3$) 2950 (ν_{CH}), 2385 (ν_{BH}), 1660 (ν_{CO}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.72 (s, $(CH_3)_3N$), 3.48 (s, OCH_3); ^{11}B NMR ($CDCl_3$, $(C_2H_5)_2O{\cdot}BF_3$) δ −9.09 (J_{B-H} = 99 Hz). Anal. Calcd for $C_5H_{14}BNO_2$: C, 45.85; H, 10.77; N, 10.69. Found: C, 45.95; H, 10.99; N, 10.56.

A similar reaction was carried out with $(CH_3)_3N{\cdot}BH_2COOH$ (11.2 g, 0.109 mol) and DCC (27 g, 0.131 mol, 20% excess) in CH_3OH (250 mL) for 2 weeks at ambient temperature. After similar workup, the crude product was purified by vacuum sublimation at 100 °C to give **2** (14 g, 98%).

Preparation of $(CH_3)_2NH{\cdot}BH_2COOCH_3$ (3). Anhydrous $(CH_3)_2NH$ (50 g, 1.1 mol) was cooled to 0 °C and poured into a glass pressure reaction vessel containing $(CH_3)_3N{\cdot}BH_2COOCH_3$ (**2**) (6 g, 0.046 mol) maintained at 0 °C. The vessel was assembled and stored at ambient temperature for 2 weeks with occasional shaking each day. The reaction veseel was then cooled to 0 °C and opened slowly. Pentane (ca. 80 mL) and CH_2Cl_2 (50 mL) were added to the solution, and the excess volatile amines were allowed to evaporate off. The remaining amines and solvent were removed by rotary evaporation. The thick liquid thus obtained solidified on standing and contained ca. 8% of unreacted ester **2** (by ^{1}H NMR). The mixture was dissolved in CH_2Cl_2, treated with $MgSO_4$ and activated charcoal, and then filtered over Celite. Removal of the solvent gave 5.4 g of a brown oily material, which was taken up in CH_2Cl_2, washed with water (2

(10) The ammonia-exchange reaction was carried out in a stainless steel pressure vessel obtained from Pope Scientific, Inc., Menomonee Falls, WI.

× 60 mL), and dried over $MgSO_4$. After removal of the solvent, pure solid ester (3.6 g, 67.1%) was obtained. An analytical sample was prepared by recrystallization from diethyl ether at −78 °C: mp 52–53 °C; IR ($CDCl_3$) 2940 (ν_{CH}), 2380 (ν_{BH}), 1660 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5 (d, $(CH_3)_2N$), 3.5 (s, OCH_3); ^{11}B NMR ($CDCl_3$, $(C_2H_5)_2O{\cdot}BF_3$) δ −12.57 (t, J_{B-H} = 95 Hz). Anal. Calcd for $C_4H_{12}BNO_2$: C, 41.08; H, 10.34; N, 11.98. Found: C, 41.25; H, 10.32; N, 11.88.

Preparation of $CH_3NH_2{\cdot}BH_2COOCH_3$ (4). A solution of $CH_3NH_2{\cdot}BH_2COOH$[7] (1.68 g, 0.019 mol) and DCC (4.29 g, 0.021 mol, 10% excess) in anhydrous CH_3OH (100 mL) was stirred at ambient temperature for 6 days. The initially clear solution subsequently became cloudy, and to the resulting suspension was added H_2O (ca. 100 mL). The entire mixture was then filtered and washed with CH_2Cl_2 (3 × 50 mL). The residue resulting from evaporation of the CH_3OH/H_2O portion under reduced pressure was taken up in diethyl ether and placed in a freezer. Crude ester **4** precipitated and was recrystallized from CH_2Cl_2/pentane (3:1) in a freezer. Finally, the crystalline ester was washed with a small portion of cold water to yield 0.41 g (21%) of **4**: mp 56–57 °C; IR (Nujol) 2400 (ν_{BH}), 1650 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (t, $(CH_3)_3N$), 3.57 (s, OCH_3), 4.35 (broad s, NH_2); ^{11}B NMR ($CDCl_3$, $(C_2H_5)_2O{\cdot}BF_3$) δ −16.22 (t, J_{B-H} = 98 Hz). Anal. Calcd for $C_3H_{10}BNO_2$: C, 35.01; H, 9.79; B, 10.50; N, 13.61. Found: C, 35.22; H, 9.67; B, 10.27; N, 13.62.

Preparation of $(CH_3)_3N{\cdot}BH_2COOCH_2CH_2Cl$ (5). A solution of $(CH_3)_3N{\cdot}BH_2COOH$ (5.85 g, 0.5 mol), $HOCH_2CH_2Cl$ (4.03 g, 0.5 mol), and DCC (10.32 g, 0.5 mol) in CH_2Cl_2 (200 mL) was stirred at ambient temperature for 1 week. The resulting insoluble DCU was filtered out, and additional CH_2Cl_2 (50 mL) was added to the filtrate, which was then washed with water (3 × 50 mL). The organic portion was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The oily product was then vacuum pumped, and some DCU was filtered out. This process was repeated several times until all DCU was removed and semisolid ester **6** (6 g, 61%) was obtained: IR ($CDCl_3$) 3100 (ν_{CH}), 2400 (ν_{BH}), 1660 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (s, $(CH_3)_3N$), 3.7 (t, CH_2Cl), 4.7 (t, OCH_2); ^{11}B NMR ($CDCl_3$, $(C_2H_5)_2O{\cdot}BF_3$) δ −8.75 (t, J_{B-H} = 97 Hz).

Preparation of $H_3N{\cdot}BH_2COOCH_3$ (6). Anhydrous NH_3 condensed into a stainless-steel pressure reaction vessel containing $(CH_3)_3N{\cdot}BH_2COOCH_3$ (**2**) (3.69 g, 0.0282 mol) maintained at −78 °C. The vessel was assembled and stored at ambient temperature for 1 week, following which it was vented of excess NH_3 under N_2. The yellow residue obtained was first washed with CH_2Cl_2 (3 × 50 mL) and then dissolved in CH_3OH (50 mL). The resulting solution was treated with activated charcoal and filtered over Celite, and CH_3OH was removed under reduced pressure to yield solid **6** (1.24 g, 49% pure by ^1H and ^{11}B NMR). An analytical sample was obtained by recrystallization from methanol/diethyl ether/petroleum ether at −30 °C: mp 92–93 °C; IR (KBr disk) 2370 (ν_{BH}), 1660 (ν_{CO}) cm^{-1}; ^1H NMR (D_2O) δ 3.57 (s, OCH_3); ^{11}B NMR (D_2O, $(C_2H_5)_2O{\cdot}BF_3$) δ −20.47 (t, J_{B-H} = 94 Hz). Anal. Calcd. for $C_2H_8BNO_2$: C, 27.02; H, 9.07; N, 15.76. Found: C, 27.04; H, 9.05; N, 15.66.

Preparation of $(CH_3)_3N{\cdot}BH_2COOSi(CH_3)_3$ (7). To a 250-mL three-necked flask equipped with a condenser, dropping funnel, magnetic stirrer, nitrogen inlet, and oil bubbler were added $(CH_3)_3N{\cdot}BH_2COOH$ (5.85 g, 0.050 mol) and diethyl ether (150 mL). The slurry was cooled to 0 °C, and 2.45 M n-C_4H_9Li in hexane (20.4 mL, 0.050 mol) was added slowly under N_2. The resulting mixture was stirred at room temperature for 1 h. Freshly distilled $(CH_3)_3SiCl$ (6.4 mL, 0.050 mol) was then added slowly to the mixture, which was stirred at room temperature overnight and filtered under N_2, and the solvent was removed under reduced pressure. Finally, the crude silyl ester was vacuum distilled to give a clear moisture-sensitive liquid that solidified on standing (5.5 g, 58%): bp 60 °C (0.2 torr)); IR (neat) 2875 (ν_{CH}), 2380 (ν_{BH}), 1640 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, $(CH_3)_3Si$), 2.68 (s, $(CH_3)_3N$). Anal. Calcd for $C_7H_{20}BNO_2Si$: C, 44.45; H, 10.66; B, 5.72; N, 7.41. Found: C, 44.71; H, 10.59; B, 5.81; N, 7.41.

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