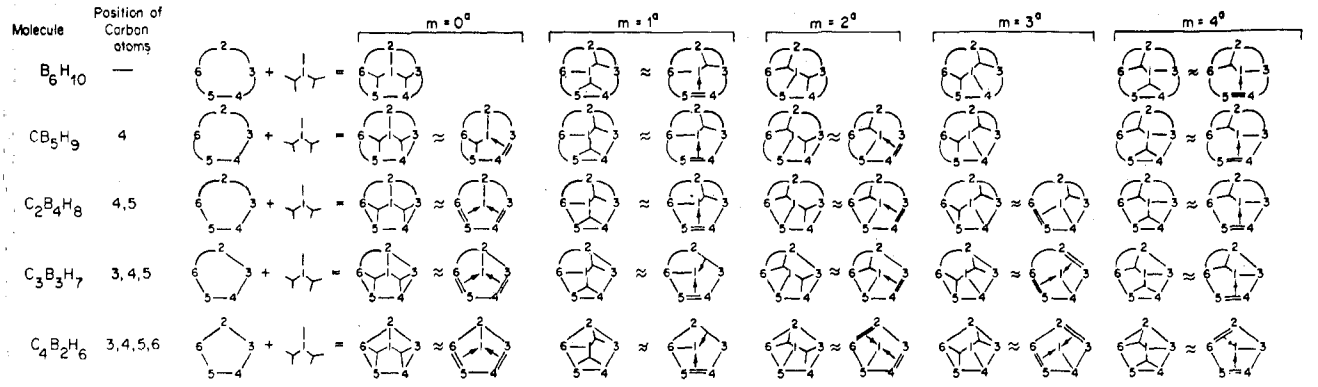
TABLE XI

VALENCE STRUCTURES FOR NEUTRAL CARBORANES RELATED TO B_6H_{10}



[a] The unit is rotated by 2πm/5 before being added to the pentagonal base unit.

pressed as a combination of the "equivalent" structures of columns 1 and 4. In $C_3B_3H_7$,[34] the preferred structures are probably those in columns 2 and 4, which minimize the formal charges. The situation in the recently prepared $C_4B_2H_6$[35] is less clear, but formal charge considerations suggest a preference for either the structures of column 0 or the equivalent pair, columns 1 and 4. The suggestion here of a π-donation model involving two double bonds would make a structural determination and comparison of C–C and C–B bond distances in this molecule extremely interesting.

(34) C. L. Bramlett and R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 4269 (1966).

(35) T. P. Onak and G. T. F. Wong, *ibid.*, in press; T. P. Onak, private communication, 1970.

The formalism developed above may also be applied to borane or carborane ions of the above species, such as $B_6H_9^-$ [36] or $B_4C_2H_7^-$.[37] An ion produced by removal of a proton from a bridge position is simply assigned those resonance structures of the parent isostructural carborane which minimize the formal charges.

Acknowledgments.—We wish to thank the National Science Foundation for predoctoral fellowships to I. R. E., J. A. T., and E. S. and the Office of Naval Research for financial support of this work.

(36) H. D. Johnson, II, Ph.D. Thesis, The Ohio State University, 1969; *Diss. Abstr.*, in press.

(37) T. P. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

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Reaction of Amino Acid Derivatives with Trihaloboranes and with Sodium Borohydride

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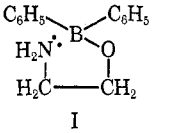
The borane, trichloroborane, and some trifluoroborane adducts of several amino acid esters were prepared. The nmr and ir spectra show them all to be amine adducts. The BF_3 adducts of methyl glycinate and of methyl β-alaninate were converted to the corresponding N-substituted borazines. Possible intramolecular coordination of ring borons by carbonyl groups in the N substituent was investigated but none could be observed. The reaction of BCl_3 with glycine gave the novel compound $B(O_2CCH_2NH_3^+)_3(BCl_4^-)_3$.

Introduction

The intramolecular coordination of a boron atom to give a four-coordinate species has been shown in many cases to result in a material that is often much more resistant to hydrolysis than is a similar three-coordinate compound. Diphenylborinic acid is very difficult to obtain, but its β-aminoethyl ester, I, has been isolated and found to be very resistant to hydrolysis.[1] This has been attributed to intramolecular coordination of the



I

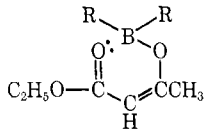
* To whom correspondence should be addressed.

(1) R. L. Letzinger and I. Skoog, *J. Amer. Chem. Soc.*, **77**, 2491 (1955).

TABLE I
ANALYTICAL DATA

Compound	Mp, °C	% calcd					% found				
		C	H	B	Cl	N	C	H	B	Cl	N
$CH_3OC(O)CH_2N(CH_3)_2 \cdot BCl_3$	92–94	25.82	4.69	4.61	45.40	5.98	25.75	5.03	4.87	44.73	5.98
$CH_3OC(O)CH_2NH_2 \cdot BCl_3$	53–55	17.46	3.39	5.24	51.45	6.79	17.83	3.96	4.70	51.21	7.08
$CH_3OC(O)CH_2NH_2 \cdot BF_3$	90–91	25.57	5.01	7.67		9.94	24.55	5.09	6.92		10.02
$CH_3OC(O)CH_2CH_2NH_2 \cdot BF_3$	Oil	28.71	5.31	6.32		8.20	29.66	6.41	5.81		8.86
$CH_3OC(O)CH_2NH_2 \cdot BH_3$	70–71	35.01	9.79	10.50		3.61	35.81	9.11	10.14		3.33
$CH_3OC(O)CH_2N(CH_3)_2 \cdot BH_3$	24–26	45.85	10.77	8.25		10.70	43.16	10.31	8.29		10.60
$C_2H_5OC(O)CH_2NH_2CH_3^+,BCl_4^-$	Oil	22.88	4.47	3.99	52.37	5.17	21.35	4.59	4.54	52.00	5.17
$(FBNCH_2CH_2C(O)OCH_3)_3$	42–45	36.70	5.39	8.26		10.70	37.37	6.05	8.45		9.87
$CH_3CN \cdot B(OC(O)CH_2NH_3^+,BCl_4^-)_3$	95–100			5.28	51.96				5.16	48.92	

boron by nitrogen giving a five-membered ring. Carbonyl groups may also act as ligands and coordinate boron.[2,3] When dialkylchloroboranes (R_2BCl) are treated with ethyl acetoacetate, they give compounds of unusual hydrolytic and oxidative stability, II. Stability has been attributed to ring formation and resonance.



II

Also of interest is the reaction of trichloroborane with carboxylic acids. If acetic acid is treated with BCl_3 in chloroform, the product obtained is $(AcO)_2BOB(OAc)_2$, in which the borons are coordinated by carbonyl oxygens.[4,5] If the same reaction is carried out in dioxane, the product obtained is $diox \cdot B(OAc)_3$.[6] In this species the fourth position on the boron is taken by the solvent.

We decided to attempt the preparation of some borazines which contained carbonyl groups in the nitrogen substituent and to determine whether or not the oxygen would coordinate the ring borons and thus have any effect on the hydrolysis of the borazine.

Because they had not been previously reported, we first prepared the borane and some trihaloborane adducts of several amino esters in order to establish the donor atom. This was required because trihaloboranes are capable of forming adducts with carbonyl groups as well as with amines.

Esters were employed because the use of amino acids would lead to borates. The methyl esters of glycine, β-alanine, and *N*,*N*-dimethylglycine and the ethyl ester of *N*-methylglycine (sarcosine) were used.

The boranes formed amine adducts in all cases, including the two primary amino esters, methyl glycinate and methyl β-alaninate, thus allowing the possibility for their conversion to the corresponding N-substituted borazines by various routes such as pyrolysis and addition of triethylamine, etc. The standard preparative methods for borazines are somewhat limited when using amino esters in place of alkyl- or arylamines. Sodium borohydride and diborane are capable of reducing esters and trichloroborane cleaves ester groups.[7]

If the borazines are obtained and intramolecular coordination occurs, the two primary amino esters studied would result in five- and six-membered side rings, the most favorable size for ring systems.

Experimental Section

Materials.—Methyl glycinate hydrochloride, methyl β-alaninate hydrochloride, and ethyl sarcosinate hydrochloride were prepared from the respective amino acids *via* the Fischer esterification, using excess hydrogen chloride.

Since the neutral amino esters rapidly peptize, they had to be prepared immediately before using. This was done by bubbling ammonia through a diethyl ether slurry of the amino ester hydrochloride at 0°, filtering the NH_4Cl, and vacuum distilling the ester.[8] Boiling points are as follows: $CH_3O_2CCH_2NH_2$, bp 31° (6 mm), lit.[8] bp 45° (20 mm); $CH_3O_2CCH_2CH_2NH_2$, bp 31° (5 mm), lit.[9] bp 58° (15 mm); $CH_3CH_2O_2CCH_2NHCH_3$; bp 48° (10 mm), lit.[10] bp 60° (25 mm).

Methyl *N*,*N*-dimethylglycinate was prepared by the reaction of methyl chloroacetate with dimethylamine, bp 36° (8 mm), lit.[9] bp 51° (12 mm).

Spectra.—Nmr spectra were obtained on a Varian HA-100 spectrometer, the proton spectra at 100 MHz and boron at 32.1 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 457 or a Beckman IR-5A spectrophotometer.

Trichloroborane Adducts.—Samples of the amino esters on the order of 1 g were dissolved in CH_2Cl_2 or $CHCl_3$ and BCl_3

TABLE II
^1H NMR OF TRIHALOBORANE ADDUCTS

Compound	Group	Chemical shift, ppm	Coupling, Hz
$CH_3OCCH_2N(CH_3)_2 \cdot BCl_3$ ($CHCl_3$)	$-N(CH_3)_2$	3.25	q, 2.8
	CH_2-	4.24	b
	$-OCH_3$	3.82	s
$CH_3OCCH_2NH_2 \cdot BF_3$ (CH_3CN)	$-NCH_2-$	3.61	t, 4
	$-OCH_3$	3.79	s
	$-NH_2$	5.15	b
$CH_3OCCH_2CH_2NH_2 \cdot BF_3$ (CH_2Cl_2)	$-OCH_3$	3.69	s
	$-CH_2CH_2-$	2.69	t, 6.3
	$-NCH_2CH_2-$	3.16	t, 6.3
	$-NH_2$	5.87	b

(2) W. Gerrard, M. F. Lappert, and R. Shepperton, *J. Chem. Soc.*, 3648 (1958).
(3) E. Muetterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.
(4) L. A. Duncanson, *et al.*, *J. Chem. Soc.*, 3652 (1958).
(5) W. Gerrard and M. A. Wheelans, *Chem. Ind. (London)*, 758 (1954).
(6) H. V. Ribbel, *Z. Anorg. Allg. Chem.*, **359**, 203 (1968).
(7) M. Frazer and W. Gerrard, *J. Chem. Soc.*, 2959 (1955).
(8) M. Franckel and E. Kalchaliki, *J. Amer. Chem. Soc.*, **64**, 266 (1942).
(9) B. J. Heilbron, Ed., "Directory of Organic Compounds," Oxford Press, New York, N. Y., 1946.
(10) E. A. Pritt and S. M. McElvain, *J. Amer. Chem. Soc.*, **55**, 1233 (1933).

TABLE III

^{1}H NMR OF BORANE ADDUCTS

Compound	Group	Chemical shift, ppm	Coupling, Hz
$CH_3OCCH_2NH_2\cdot BH_3$ (CH_2Cl_2)	$-CH_2-$	3.61	t, 7
	$-OCH_3$	3.79	s
	$-NH_2$	4.46	b
	$-BH_3$	Not obsd	
$CH_3CH_2OCCH_2NHCH_3\cdot BH_3$ (CH_2Cl_2)	$-CH_2CH_3$	1.29	t, 7.2
	$-NCH_3$	2.59	d, 6
	$-NCH_2-$	~3.5	AB
	$-CH_2CH_3$	4.25	q, 7.2
	$-NH$	4.90	b
	$-BH_3$	Not obsd	
$CH_3OCCH_2N(CH_3)_2\cdot BH_3$ (CH_2Cl_2)	$-N(CH_3)_2$	2.83	s
	$-NCH_2-$	3.66	s
	$-OCH_3$	3.76	s
	$-BH_3$	Not obsd	

TABLE IV

^{1}H NMR OF AMINO ESTER HYDROTETRACHLOROBORATES

Compound	Group	Chemical shift, ppm	Coupling, Hz
$CH_3OCCH_2NH_3^+,BCl_4^-$ (CH_3CN)	$-OCH_3$	3.81	s
	$-CH_2-$	3.82	q, 5.8
	$-NH_3^+$	6.64	b
$CH_3CH_2OCCH_2NH_2CH_3^+,BCl_4^-$ (CH_3CN)	$-CH_2CH_3$	1.28	t, 7.0
	$-NCH_3$	2.73	t, 7.5
	$-NCH_2-$	3.83	t, 7.5
	$-CH_2CH_3$	4.27	t, 7.0
	$-NH_2^+$	7.35	b
$B(OCCH_2NH_3^+,BCl_4^-)_3$ (CH_3CN) (from glycine)	$-CH_2-$	3.78	q, 5.3
	$-NH_3^+$	6.51	b
$B(OCCH_2NH_3^+,BCl_4^-)_3$ (CH_3CN) (from glycine hydrochloride)	$-CH_2-$	3.74	q, 5.3
	$-NH_3^+$	6.50	b

was condensed onto the frozen solutions at −196°. $CH_3OC(O)CH_2N(CH_3)_2\cdot BCl_3$ gave a yellow solution. Removal of the solvent and extraction of the solids with benzene gave a pure product. $C_2H_5OC(O)CH_2NHCH_3\cdot BCl_3$ rapidly disproportionated. Spectra were obtained, but no sample for analysis could be isolated. The adducts may also be prepared using the solid adduct $CH_3CN\cdot BCl_3$ instead of gaseous BCl_3.

Trifluoroborane Adducts.—Freshly distilled amino esters were dissolved in diethyl ether at −20° under an N_2 cover and $(C_2H_5)_2O\cdot BF_3$ was slowly added causing the formation of a white oil. The ether was decanted and the product was reprecipitated from CH_2Cl_2 to remove any $(C_2H_5)_2O\cdot BF_3$. Pumping on the oils sometimes caused them to change to solids but usually the solids reverted to oils on standing.

Borane Adducts.—The amino ester hydrochloride and $NaBH_4$ were refluxed overnight in monoglyme under an N_2 cover. A slight excess of $NaBH_4$ was used. The hot reaction solution was filtered under N_2. Removal of the solvent left a white solid.

TABLE V

^{1}H NMR OF BORAZINES

Compound	Group	Chemical shift, ppm	Coupling, Hz
$(FBNCH_2COCH_3)_3$ (CH_2Cl_2)	$-OCH_3$	3.71	s
	$-CH_2$	3.89	s
$(FBNCH_2CH_2COCH_3)_3$ (CH_2Cl_2)	$-NCH_2CH_2$	2.47	t, 7
	$-NCH_2CH_2-$	3.40	t, 7
	$-OCH_3$	3.64	s

TABLE VI

^{11}B NMR SPECTRA

Compound	Chemical shift *vs.* $(C_2H_5)_2O\cdot BF_3$, ppm	Coupling, Hz
$CH_3OCCH_2NH_3^+,BCl_4^-$ (CH_3CN)	−6.6	s
$CH_3CH_2OCCH_2NH_2CH_3^+,BCl_4^-$ (CH_2Cl_2)	−6.5	s
$CH_3CN\cdot B(OCCH_2NH_3^+,BCl_4^-)_3$ (CH_3CN)	−6.1	s
	−5.0	s
$CH_3OCCH_2NH_2\cdot BH_3$ (CH_2Cl_2)	+17.5	q, 96
$CH_3CH_2OCCH_2NHCH_3\cdot BH_3$ (CH_2Cl_2)	+13.6	q, 96
$CH_3OCCH_2N(CH_3)_2\cdot BH_3$ (CH_2Cl_2)	+6.8	q, 96
$(FBNCH_2CH_2COCH_3)_3$ (CH_2Cl_2)	−35.7	s

$C_2H_5OC(O)CH_2NHCH_3\cdot BH_3$ was prepared in this manner, but no sample suitable for analysis was obtained. $CH_3OC(O)CH_2N(CH_3)_2\cdot BH_3$ was prepared by adding B_2H_6 to a chloroform solution of the amino ester at −196°.

All the amino ester adducts showed uncoordinated carbonyl stretch at 1720–1740 cm^{-1}. The borane adducts all showed B–H stretches at 2250–2350 cm^{-1}.

Tetrachloroborates.—Acetonitrile–trichloroborane (0.9160 g, 5.789 mmol) and methyl glycinate hydrochloride (0.7282 g, 5.793 mmol) were placed in a flask with a stirring bar and put on a vacuum line, and the flask was evacuated. Thirty milliliters of CH_3CN was condensed onto the solids at −196°. On warming to room temperature all the solids dissolved. Removal and fractionation of the solvent showed no HCl to have been evolved. The solid product left after removal of solvent melted at 53–55°, but accurate analysis could not be obtained. Since the BCl_4^- salt is soluble in CH_3CN, in which $CH_3OC(O)CH_2NH_3^+,Cl^-$ is insoluble, larger amounts of the product were prepared by treating excess amino ester hydrochloride with $CH_3CN\cdot BCl_3$ under N_2, filtering, and recovering the product from the filtrate.

$C_2H_5OC(O)CH_2NH_2CH_3^+,BCl_4^-$ was prepared in CH_2Cl_2 from the corresponding hydrochloride salt and BCl_3. The BCl_4^- salt is somewhat soluble in CH_2Cl_2.

Both products reported showed strong absorptions in the ir spectrum at 665 and 690 cm^{-1} (BCl_4^-).

$CH_3CN \cdot B(OC(O)CH_2NH_3^+,BCl_4^-)_3$.—Acetonitrile–trichloroborane (0.3324 g, 2.108 mmol) and glycine (0.1183 g, 1.576 mmol) were mixed in a 50-ml flask. The flask was placed on a vacuum line and evacuated, and 25 ml of CH_3CN was condensed in at −196°. On warming to room temperature all the solids dissolved. Fractionation of the solvent through traps at −78, −126, and −196° showed no HCl.

A reaction was performed as above using glycine hydrochloride (0.2754 g, 2.47 mmol) and $CH_3CN \cdot BCl_3$ (0.5208 g, 3.29 mmol). Fractionation of the solvent as above gave 2.36 mmol of a gas identified as HCl. The products obtained from glycine and from glycine hydrochloride were shown to be identical by their melting point (95–100°), ir [1720 (C=O), 665, and 690 cm^{-1} (BCl_4^-)], ^{11}B and ^1H nmr, and analysis. Although analytical data are not in close agreement with the proposed adduct, the B:Cl ratio is that expected for the proposed tetrachloroborate.

Trifluoroborazine.—$(FBNCH_2CH_2CO_2CH_3)_3$ was prepared by mixing $CH_3OC(O)CH_2CH_2NH_2$ (8.364 g, 0.08 mol) and $(i\text{-}C_3H_7)_2NC_2H_5$ (20.756 g, 0.161 mol) in benzene and slowly dropping in a benzene solution of $(C_2H_5)_2O \cdot BF_3$ (34.191 g, 9.241 mol).[11] On the addition heat was evolved, a solid formed, and the solution turned yellow. The mixture was stirred at room temperature for 15 hr. Filtration and removal of the solvent left a light brown oil. The oil was reprecipitated from CH_2Cl_2 with hexane. On one occasion a solid formed which later reverted to an oil. Ir spectrum (film): 1730 (C=O), 1490–1450 (BN), 1200–1170 (BF), and 720 cm^{-1} (BN); strong absorption also at 720 cm^{-1}. Mass spectrum (70 eV) *m/e* (relative intensity): 374 (1), 320 (1), 91 (59), 92 (46), 73 (41), 61 (42), 43 (55), 44 (55), 29 (74), 30 (94), 31 (100), 15 (63).

$(FBNCH_2CO_2CH_3)_3$ was prepared as above using freshly prepared methyl glycinate. Pure samples of product could not be obtained. Ir spectrum (film): 1730 (C=O), 1490–1440 (BN), 1200–1150 (BF), and 760 cm^{-1} (BN). Mass spectrum (70 eV) *m/e* (relative intensity): 352 (1), 292 (61), 175 (39), 91 (65), 84 (74), 73 (65), 61 (61), 59 (61), 49 (100), 30 (83), 15 (60).

The fragments reported are those of large relative intensity, those matching in the spectra of the two borazines or those attributable to ions expected from a borazine with an ester side group. Each of the mass spectra contains several hundred peaks, presumably due to thermal decomposition as well as fragmentation. It did not appear valid to assign peaks on the basis of differences in boron isotope content.

Attempted Preparation of $(ClBNCH_2CO_2CH_3)_3$ and of $(HBNCH_2CO_2CH_3)_3$.—Numerous attempts were made to prepare the N-substituted *B*-trichloroborazine from $CH_3OC(O)CH_2NH_2 \cdot BCl_3$ and from $CH_3OC(O)CH_2NH_3^+,BCl_4^-$ by heating and/or addition of $(C_2H_5)_3N$ in a variety of solvents. However, in each case only $(C_2H_5)_3NH^+Cl^-$ and/or a black, tarry material resulted.

As might have been expected, refluxing $CH_3OC(O)CH_2NH_3^+$, Cl^- with $NaBH_4$ in diglyme apparently reduced the ester. White needles formed in the relux condenser, mp 43–46°. Nmr spectrum ($CHCl_3$): δ 3.45 (s, ?). Ir spectrum ($CHCl_3$): 1475 (BN?) and 1335 cm^{-1} (BO?); no (C=O) or (BH) frequencies. No desired product could be obtained by pyrolysis of $CH_3OC(O)CH_2NH_2 \cdot BH_3$, either with or without solvents.

Discussion

Adducts.—The adducts of $(CH_3)_2NCH_2CO_2CH_3$ were prepared first in order to establish the donor site. A tertiary amino ester was chosen since they are the least moisture sensitive and are not prone to decomposition. The coupling of ^{11}B (spin $^3/_2$) with the $N(CH_3)_2$ group giving rise to a 1:1:1:1 quartet for the methyl proton shows nitrogen unquestionably to be the donor atom. This coupling occurs only with BCl_3. Neither the BH_3 nor BF_3 adduct shows coupling of boron with the *N*-methyl protons. This same pattern of coupling has been observed for the same three borane adducts of trimethylamine.[12] All three adducts exhibit considerable deshielding of the *N*-methyl and *N*-methylene protons in the order $BCl_3 > BF_3 \sim BH_3$. The methoxy protons being six bonds removed are only slightly affected by adduct formation. The ir spectra confirm that no carbonyl adduct is formed, since there is no change in carbonyl stretching frequency. Ethyl acetate shows a shift of 170 cm^{-1} in its carbonyl stretch on addition of BCl_3.[13]

The secondary amino ester adducts are by far the least stable. $Cl_3B \cdot CH_3HNCH_2CO_2C_2H_5$ could never be isolated, probably because of rapid disproportionation to an aminoborane and a tetrachloroborate. Absorptions were noted in the ir arising from a BCl_4^- species. The borane adduct, $H_3B \cdot CH_3HNCH_2CO_2C_2H_5$, was isolated, but it slowly evolved a gas, probably hydrogen.

The amine–borane section of $H_3B \cdot CH_3HNCH_2CO_2C_2H_5$ exhibits an interesting nmr spectrum (Figure 1). The CH_3 group appears as a doublet because

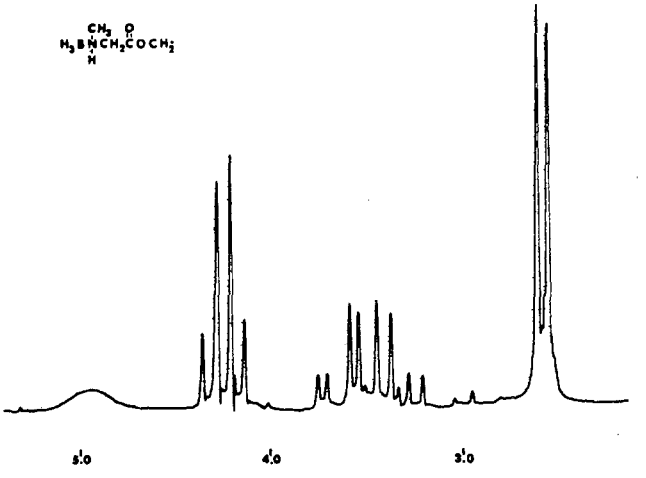


Figure 1.—The ^1H nmr spectrum of ethyl sarcosinate–borane.

of coupling with the amine proton. No splitting by the boron is observed. The N–CH_2– group is adjacent to an asymmetric nitrogen and as a result the two hydrogens are nonequivalent, coupling with one another as well as with the amine proton giving the eight peaks of the AB portion of an ABX spectrum. On inspection of the spectrum of the BCl_3 adduct of ethyl sarcosinate in which ^{11}B coupling is observed a very interesting phenomenon is noted (Figure 2). The N–CH_3 group appears as a septet. This arises from coupling with boron (spin $^3/_2$), J_{BH} = 2.8 Hz, and with the amine proton, J = 5.6 Hz. The two patterns overlap giving only six instead of eight peaks. The nitrogen atom having four different groups attached is again asymmetric and the two N–CH_2 protons nonequivalent. The high-field half of the AB pattern consists of four peaks as does the same portion of the borane adduct

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(13) M. F. Lappert, *J. Chem. Soc.*, 817 (1961).

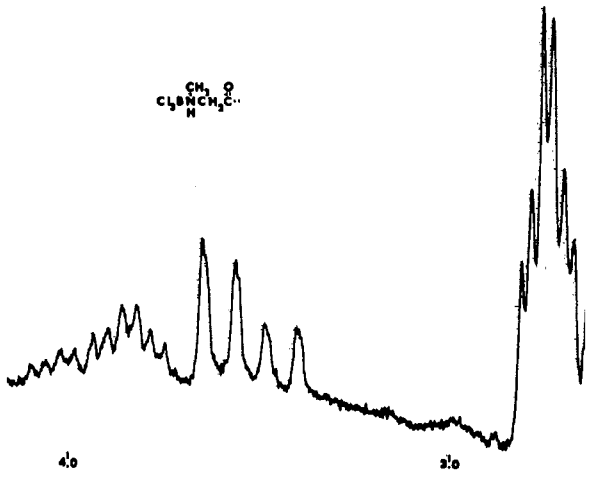

Figure 2.—The ^1H nmr spectrum of ethyl sarcosinate–trichloroborane *N*-methylene and *N*-methyl groups.

spectrum. However the low-field half consists of two sextets as a result of coupling of one of the methylene hydrogens with boron as well as with the amine hydrogen.

The primary amino ester adducts show a narrow solubility range; in fact no solvent was found for $Cl_3B \cdot H_2NCH_2CO_2CH_3$. It reacted violently with protic solvents. The BF_3 adducts of methyl glycinate and of methyl β-alaninate and the borane adduct of methyl glycinate have some solubility in solvents usable for spectra. The spectra show them to be amine adducts; thus the path to possible conversion to the corresponding borazines is open.

Another route to *N*-substituted-*B*-trichloroborazines is *via* the ammonium tetrachloroborates. In this work the use of amino ester hydrochlorides to form tetrachloroborates and then the borazines would have been convenient since the neutral amino esters are unstable and must be prepared each time a reaction is to be run. The inability to convert these salts to the trichloroborazines was probably caused by the reactivity of some boron chloride species toward the carbonyl groups. Ester groups are readily cleaved by trichloroborane.[14]

The reactions of glycine (eq 1) and of glycine hydrochloride (eq 2) with BCl_3 both give the same product.

$$4BCl_3 + 3H_2NCH_2CO_2H \xrightarrow{CH_3CN} B(O_2CCH_2NH_3)_3^{3+} + 3BCl_4^- \quad (1)$$

$$4BCl_3 + 3Cl^-,H_3^+NCH_2CO_2H \xrightarrow{CH_3CN} B(O_2CCH_2NH_3)_3^{3+} + 3BCl_4^- + 3HCl \quad (2)$$

Only with glycine hydrochloride is HCl liberated. Varying the ratio of BCl_3 to glycine hydrochloride gave amounts of HCl predicted by eq 2. The ^{11}B nmr of acetonitrile solutions of the product showed two kinds of boron in approximately a 3:1 ratio. The larger peak at −6.1 ppm is due to BCl_4^-. The smaller peak at −5.0 ppm must arise from the borate boron. Both signals are in the range of boron resonances in which tetrahedrally coordinated boron is found. An ir spectrum in KBr of the solid obtained on removing the solvent showed a C–N stretch at 2350 cm^{-1} which indicates coordination by the nitrile group. The C–N stretch of pure acetonitrile is 2270 cm^{-1}, while in $CH_3CN \cdot BCl_3$ it is 2400 cm^{-1}.[15]

Trifluoroborazines.—The only borazines that were prepared are the two trifluoroborazines derived from methyl glycinate and methyl β-alaninate. They were produced using the method recently described by Harris and Rudner.[11] Their method is especially suitable to these systems for several reasons. Trifluoroborane is much less reactive toward carbonyl groups than is BCl_3 and does not have the reducing properties of BH_3. The ability to convert the adducts to the borazine by a method not requiring heating is favorable since it is less destructive of the amino esters.

The trifluoroborazines were prepared a number of times and in each instance $(FBNCH_2CH_2CO_2CH_3)_3$ was obtained in purer form than was $(FBNCH_2CO_2CH_3)_3$.

On comparison of the nmr spectrum of $F_3B \cdot H_2NCH_2CH_2CO_2CH_3$ with that of $(FBNCH_2CH_2CO_2CH_3)_3$ it is noted that in the borazine the triplet arising from the methylene group α to the nitrogen is deshielded by 0.24 ppm while the β-methylene is shielded by 0.22 ppm as compared to the adduct. This phenomenon is usually associated with groups substituted on aromatic rings.

The mass spectra of the two trifluoroborazines were run only as an aid in identifying the compounds and no detailed mass spectral study was intended. The spectra were run with inlet and oven temperatures of 210° which may have caused some thermal decomposition. Each of the spectra contains several hundred peaks, so only the more abundant fragments or peaks corresponding to obvious fragments are reported. There were five fragments of large relative abundance appearing in both spectra: 15 (CH_3), 30 (BF), 61 (CH_2COF?), 73 ($CH_2CO_2CH_3$), and 91 (CH_2COBF_2?). The base peak for $(FBNCH_2CO_2CH_3)_3$ was at *m/e* 49 (BF_2?). The spectrum also contained a small peak at 352, the parent ion, and a large peak at 292 which is P − CO_2CH_3. The loss of an ester group is the primary mode of fragmentation for α-amino esters.[16] The base peak for the other borazine was at *m/e* 31 (OCH_3 and/or HBF). The heaviest mass peak observed was 394 (P − F?).

A comparison of the ir spectra of CH_2Cl_2 solutions of $F_3B \cdot H_2NCH_2CH_2CO_2CH_3$ and $(FBNCH_2CH_2CO_2)_3$ shows no change in carbonyl stretching frequencies. This would seem to indicate the lack of any association between the carbonyl group and a ring boron. The ^{11}B chemical shift of −35.7 ppm also is indicative of a fluoroborazine and not of a four-coordinate boron.

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