New Azoniaboratacyclopropanes from $(F_3C)_2BNMe_2$ and Diazomethane Derivatives – Structure of *cyclo*-$(F_3C)_2B–CPh_2–NMe_2$ and $HOB(CF_3)_2–CHC_6F_5–NHMe_2$

David J. Brauer,[a] Hans Bürger,*[a] Silke Buchheim-Spiegel,[a] and Gottfried Pawelke[a]

Dedicated to Professor H. D. Lutz on the occasion of his 65th birthday

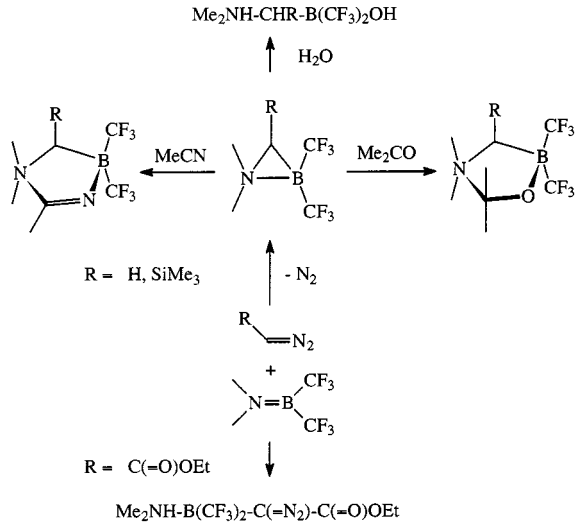
Keywords: Boron / Small rings / Trifluoromethyl group / Crystal structure

1,1-Dimethyl-2,2-bis(trifluoromethyl)azoniaboratacyclopropanes, *cyclo*-$(F_3C)_2B–CR^1R^2–NMe_2$ [$R^1 = R^2 = C_6H_5$ (**2a**); $R^1/R^2 = C_{12}H_8$ (**2b**); R^1 = H, $R^2 = C_6H_5$ (**2c**), 4-FC_6H_4 (**2d**), 3-FC_6H_4 (**2e**), 2-FC_6H_4 (**2f**), C_6F_5 (**2g**), *i*Pr (**2h**), *t*Bu (**2i**); R^1 = Me, R^2 = C(=O)OMe (**2j**), C(=O)OEt (**2k**)] have been obtained from $(F_3C)_2BNMe_2$ (**1**) and diazomethanes $R^1R^2CN_2$. In contrast to compound **2a**, the B–N bonds of **2b**–**2k** hydrolyze to form the zwitterionic species $Me_2NH–CR^1R^2–B(CF_3)_2OH$ (**3b**–**3k**). The diazoacetic acid esters $HC(N_2)C(=O)OMe$ and $HC(N_2)C(=O)OtBu$ react with **1** to form three-membered rings, which hydrolyze rapidly to form $Me_2NH–CR^1R^2–B(CF_3)_2OH$ [R^1 = H, R^2 = C(=O)OMe (**3l**), C(=O)O*t*Bu (**3m**)]. F_3CSiF_3 reacts under elimination of CF_2 with **1** to form the acyclic derivative $(F_3C)_2BF–CF=NMe_2$ (**4**). The structures of **2a** and **3g** have been investigated crystallographically. A nearly eclipsed conformation is found for the central B–C bond of **3g**, which is 0.097(7) Å longer than the B–C bond length in the three-membered ring of **2a**.

(Dimethylamino)bis(trifluoromethyl)borane, $(F_3C)_2BNMe_2$ (**1**), possesses chemical properties that are unique in aminoborane chemistry.[1] Owing to a balance of pronounced electrophilic character and steric protection of the boron atom, the reactivity of its strong B=N bond bears a degree of resemblance to an olefinic C=C bond. On the other hand its polarity is related to that of a C=N bond in a dimethyliminium cation. In a preceding paper we reported on reactions of diazomethane derivatives with **1**.[2] While diazomethane itself, trimethylsilyldiazomethane and trimethylsilyl(benzyl)diazomethane formed novel heterocyclopropane derivatives, diazoacetic acid ethyl ester underwent an ene-type reaction to form an extraordinary stable, borylated diazomethane species (Scheme 1). In contrast to the B–N bond in dimethylamine–bis(trifluoromethyl)boranes, $R(F_3C)_2B \cdot NMe_2H$, which is not only stable to dissociation but also to displacement reactions at room temperature, the B–N bond in the azoniaboratacyclopropanes, which are formed from reactions of **1** with diazomethane or trimethylsilydiazomethane, is rather reactive.

Thus, water cleaves their B–N bonds to form $Me_2NH–CHR–B(CF_3)_2OH$ while nitriles like H_3CCN or carbonyl compounds like acetone insert into the B–N bond to yield the five-membered heterocycles *cyclo*-$Me_2N–CHR–B(CF_3)_2N=CMe$ and *cyclo*-$Me_2N–CHR–B(CF_3)_2O–CMe_2$, respectively.[3] On the other hand *cyclo*-$(F_3C)_2B–C(SiMe_3)(CH_2C_6H_5)–NMe_2$ was far less reactive than the other three-membered rings.

The reasons for the varying reactivity were not fully understood, and there were questions left unanswered: (1) What is the influence of the substituents R^1 and R^2 on the formation, reactivity and stability of azoniaboratacyclopropanes? (2) Can other potential carbene sources (e. g., F_3CSiF_3) be used to form such three-membered rings? (3) Will diazoacetic acid esters other than $HC(N_2)C(=O)OEt$ also enter into ene-type reactions or will they form three-membered rings? Here we report on our results.



Scheme 1. Diazomethane derivatives and (dimethylamino)bis(trifluoromethyl)borane

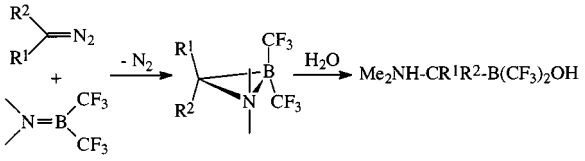
Results

The reactivity of compound **1** towards many solvents and reagents prohibits in situ generation of diazomethanes. Furthermore the diazomethanes must be accessible as neat ma-

[a] Anorganische Chemie, FB 9, Universität-GH, D-42097 Wuppertal, Germany
E-mail: buerger1@wrcs3.urz.uni-wuppertal.de

  1434–1948/99/0202–0255 $ 17.50+.50/0

terial in high purity. These demands limit the number of possible candidates to a small number of stable, isolable diazomethanes. Of these candidates, $R^1R^2CN_2$, those with R^1 and R^2 as defined in Scheme 2 were prepared and dissolved in dry pentane. Compound **1** was condensed onto these frozen solutions at −196°C. Upon warming decolorization and evolution of nitrogen was observed as soon as **1** melted and mixed with the diazomethane solutions.



	R^1	R^2	
2a	C_6H_5	C_6H_5	
2b		$C_{12}H_8$	**3b**
2c	H	C_6H_5	**3c**
2d	H	*4*-FC_6H_4	**3d**
2e	H	*3*-FC_6H_4	**3e**
2f	H	*2*-FC_6H_4	**3f**
2g	H	C_6F_5	**3g**
2h	H	*i*-Pr	**3h**
2i	H	*t*-Bu	**3i**
2j	CH_3	C(=O)OMe	**3j**
2k	CH_3	C(=O)OEt	**3k**
	H	C(=O)OMe	**3l**
	H	C(=O)O*t*-Bu	**3m**

Scheme 2. Formation of azoniaboratacyclopropanes and hydrolytic cleavage of their B−N bond

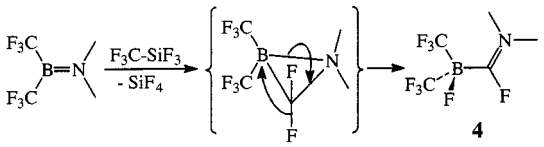
All of the investigated diazomethanes act as carbene sources, and though their reactivity towards **1** varied, no competing reactions were observed. The relatively stable diphenyldiazomethane and fluorenyldiazomethane react less rapidly than the less stable phenyl and alkyldiazomethanes. On the other hand trifluoromethyldiazomethane, F_3CHCN_2, did not react with **1**.

While $HC(N_2)COOEt$ undergoes an ene-type reaction with **1**, the corresponding diazoacetic acid esters $HC(N_2)COOMe$ and $HC(N_2)COO$*t*Bu reacted differently − three-membered rings were formed with elimination of N_2. Due to their sensitivity towards water, these ring compounds were not isolated in a pure state and therefore are missing in the list of Scheme 2. However, their hydrolysis products **3l** and **3m** were obtained in high yields.

The reactivity of **2a**−**2k** was tested by reaction with water (Scheme 2). Except for compound **2a** all of the three-membered rings hydrolyze within minutes to form the zwitterionic species **3b**−**3m**. Because neat $F_2C{=}N_2$ is difficult to prepare and because all of the diazomethanes tested here reacted as carbene sources, we were interested in testing the reactivity of a suitable difluorocarbene source with compound **1**. Such a difluorocarbene source is trifluoro(trifluoromethyl)silane, F_3CSiF_3, which is known to decompose at 30°C according to Equation 1.[4]

$$F_3C\text{-}SiF_3 \rightarrow \{CF_2\} + SiF_4 \quad (1)$$

Indeed trifluoro(trifluoromethyl)silane reacts rapidly with **1** at −60°C; however, instead of the expected three-membered ring, the acyclic isomer $(F_3C)_2BF{-}CF{=}NMe_2$ (**4**) was obtained (Scheme 3). We assume that difluorocarbene adds primarily to the B=N bond of **1**; however, the three-membered ring is unstable and rearranges by a 1,2-dyotropic shift to form **4**.



Scheme 3. Difluorocarbene and (dimethylamino)bis(trifluoromethyl)borane

Properties and Spectra

Compounds **2a**−**4** are colorless solids. Except for compound **2a** the three-membered heterocycles **2b**−**2k** are sensitive to moisture − their B−N bond being cleaved. At first it is surprising that **2a** is stable to water whereas **2b** hydrolyses readily. In both species two phenyl rings are bonded to the ring carbon atom. However, electronically both groups in the ring are different. Heterolytic breaking of the C−N bond in **2a** and **2b** would generate either a borylated diphenylmethyl (**2a**) or a borylated fluorenyl cation (**2b**). If it is accepted that the diphenylmethyl cation is more stable than the fluorenyl cation and that this is also true for a borylated species, then the $C_{13}H_8$ substituent attracts more electron density from the B−N bond in **2b** than the $C(C_6H_5)_2$ group does in **2a**. Thus, the B−N bond in **2b** is more polar than in **2a** and hence more reactive towards water.

The ^{1}H-, ^{19}F-, ^{11}B- and ^{13}C-NMR spectra of **2a**−**4** were recorded. The shift data which are set out in Table 1 are consistent with the proposed structures, and only a few comments will be necessary. The ^{13}C resonances of the CF_3 groups in **2a**−**2k** are not detectable due to quadrupolar broadening by the boron atom. In **3b**−**4** they appear as extremely broadened signals. Therefore these resonances are not included in Table 1. Compounds **2c**−**2k** and **3c**−**3m** have an asymmetric carbon atom which causes a splitting of the NMR signals of both the $N(CH_3)_2$ and $B(CF_3)_2$ groups. For compound **3g** five ^{19}F and five ^{13}C resonances are found for the pentafluorophenyl ring. This splitting is due to hindered rotation of the ring relative to the NMR time scale which was confirmed by recording the NMR spectra at different temperatures. While **2a**−**2k** show only broad signals for the ring carbon atoms, in the zwitterions **3b**−**3m** the ^{13}C resonances of these carbon atoms appear as 1:1:1:1 quadruplets with ^1J(BC) = 42−51 Hz. The ^{19}F chemical shift of the boron-bonded fluorine atom in **4** occurs at unusually high field, $\delta = -220.9$. This shift is larger than that for $Mes(F_3C)BF{-}CF{=}NMe_2$ [δ(B*F*) = −202.7][5]

Table 1. NMR-spectral data of **2a**−**2k** and **3b**−**4**[a]

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**	**2k**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**	**3l**	**3m**	**4**
^{1}H																								
δ(NC*H*$_3$)	3.00	3.02	2.48 3.04	2.46 3.02	2.51 3.04	2.86 3.03	2.65 3.09	2.77 2.82	2.82 2.91	2.81 2.96	2.85 2.99	2.64	2.59 2.74	2.62 2.77	2.91 3.00	2.88 2.99	2.73 3.02	2.76 2.88	2.88 2.99	2.86 3.10	2.64 2.93	3.16 3.25	2.93 3.08	3.35 3.60
δ(BC*H*$_n$)			3.48	3.42	3.44	3.37	3.11	1.82	2.01				3.63	3.66	3.76	4.21	4.03	2.30	2.62			3.62	3.40	
δ(CC*H*$_3$)								1.00 1.13	1.17	1.72	1.28 1.75							1.03 1.17	1.17	1.53	1.27 1.46		1.45	
δ(C*H*$_n$C)								2.05										2.15						
δ(OC*H*$_n$)										3.71	4.20									3.67	4.15	3.64		
δ(C$_6$*H*$_n$)	7.25 · 7.45	7.50 · 7.80	7.3 · 7.42	7.07 7.30	7.03 7.08 7.37 7.12 7.37	7.1 · 7.4						7.37 7.47 7.82 7.87	7.49 7.36	7.12 7.56	7.11 7.39 7.45	7.16 7.40 7.93								
δ(N*H*)												7.2	7.05	7.0	7.68	7.72	7.2	8.4	ca. 8.7	ca. 7.8	ca. 7.2	ca. 8.0	ca. 7.1	
δ(O*H*)												2.16	1.71	2.2	2.1	2.2	2.30	2.2	ca. 2.3	2.09	ca. 2.2	ca. 2	ca. 1.8	
^{19}F																								
δ(C*F*$_3$)	−55.0	−53.8	−55.5 −60.1	−55.5 −60.2	−56.0 −60.7	−56.2 −60.6	−59.6 −60.9	−57.7 −60.5	−53.1 −58.9	−58.2 −60.0	−56.1 −57.5	−65.2	−60.2 −63.7	−66.3 −69.4	−66.1 −69.4	−66.5 −69.6	−69.4 −69.5	−65.1 −68.2	−64.3 −67.3	−64.7 −67.2	−64.9 −66.8	−67.3 −70.7	−65.9 −70.4	−70.5
δ(B*F*)																								−220.9
δ(=C*F*)																								−6.6
δ(C$_6$*F*$_n$)				−112.3	−112.8	−113.1	−137.2 −151.6 −161.2							−116.3	−115.7	−117.1	−136.2 −143.0 −157.4 −164.8 −165.5							
^{11}B																								
δ(*B*)	−14.0	−11.6	−15.1	−14.6	−16.8	−16.9	−15.7	−15.5	−17.3	−17.2	−17.1	−6.6	−6.9	−6.8	−8.1	−8.0	−8.0	−9.2	−7.8	−7.4	−7.5	−3.5	−3.5	−4.1
^{13}C																								
δ(N*C*H$_3$)	45.1	45.2	41.9	41.8	42.0	41.1	41.8	40.1	41.7	42.2	42.7	41.8	41.6	41.6	42.6	42.5	44.4	38.9	ca. 42.5	41.8	42.3	41.7	41.8	40.3
			49.0	48.9	49.1	48.3	48.8	49.2	51.0	45.5	46.0		45.7	45.8	46.8	46.8	47.3	47.8	ca. 48.1	41.9		45.1	44.9	41.0
δ(B*C*)	69	65	57	56	55.8	50.7	43.6	60.7	65	ca. 55.3	ca. 55.9	75.9	68.7	67.9	69.0	59.1	57.2	70.5	74.7	70.4	70.8	62.6	63.4	ca. 189
δ(CC*H*$_3$)								20.6 23.9	30.6	15.0	14.1 15.5							21.7 24.7	30.6	11.2	11.5 14.3		27.3	
δ(*C*CH$_3$)								24.8	33.2									27.3	35.3				81.8	
δ(O*C*H$_n$)										52.2	62.2									52.4	62.9	50.7		
δ(C$_6$H$_n$)	127.5 128.5 129.5 139.1	119.8 127.1 128.8 138.3 142.5	128.6 128.8 130.7 131.9	115.6 126.5 133.8 163.0	116.0 118.8 127.7 130.2 133.1 162.6	115.0 118.6 124.5 131.3 134.3 163.4	106.1 137.9 142.0 146.7					120.8 128.0 128.1 129.7 142.8 143.3	128.9 129.2 133.7 134.0	115.6 130.4 135.8 163.8	116.3 120.9 130.5 130.9 138.0 163.8	116.5 122.4 125.1 131.7 135.9 163.5	112.3 138.4 141.4 ca. 146.2 ca. 146.9							
δ(*C*=O)										171.1	171.4									174.3	174.2	171.4	169.8	

[a] **2a**−**2h**, **2j**, **2k** in $CDCl_3$, **2i** in CD_2Cl_2, **3b**−**3d**, **3g**−**3k**, **3m**, **4** in [D_3]acetonitrile, **3e**, **3f**, **3l** in [D_6]acetone.

which was previously believed to be the upper limit for a fluorine bonded directly to boron.

EI mass-spectral data are set out in Table 2. M^+ peaks are generally weak, but the fragments [$M^+ - CF_3$] and [$M^+ - C_2F_5$] give reliable indications of the molecular mass. The base peak of the three-membered rings **2c**−**2h** is [$(CH_3)_2NCHR^+$], which is less prominent in **2i** due to the instability of the *t*Bu group. In the corresponding hydrolyzed products **3c**−**3h** the fragment [CH_3NHCHR^+] is in general the base peak.

Description of the Crystal Structures of 2a and 3g

The structure of **2a** is shown in Figure 1. The three-membered ring defines a non-crystallographic mirror plane, which is obeyed by the exocyclic bonds to within experimental error and is followed by the angles and the magnitude of the torsion angles to within 4°. The phenyl groups are oriented parallel to the B−N bond and are thus not capable of conjugation with the tangential Walsh ring orbitals.[6]

Several features of the ring geometry deserve comment. Firstly, the B−N bond length [1.568(6) Å] is clearly shorter than those reported between quaternary nitrogen atoms and $(F_3C)_2B$ entities in four-, five- and six-membered rings − all of which exceed 1.61 Å.[7−9] Secondly, the N−C(1) linkage [1.556(5) Å] is markedly longer than the N−CH_3 bonds [av. 1.484(5) Å], but examples of long bonds between quaternary nitrogen and carbon atoms have been registered in five-membered heterocycles involving the $(F_3C)_2B$ group such as *cyclo*-$(F_3C)_2B-NMe_2-CMe_2-S(=O)-O$ [1.543(3) Å[8]] and *cyclo*-$(F_3C)_2B-CH(SiMe_3)-NMe_2-CMe_2-O$ [1.582(4) Å[3]]. In this connection we note that the B−C, B−N and N−C(1) [1.556(5) Å] bond lengths in **2a** agree to within experimental error with the values [1.595(5), 1.560(5) and 1.567(4) Å] found for the corresponding linkages in *cyclo*-$(F_3C)_2B-C(SiMe_3)(CH_2C_6H_5)-NMe_2$ (**5**).[2] Thirdly, the exocyclic substituent planes of the B and C(1) atoms do not bisect the N−B−C(1) and B−C(1)−N angles, respectively, but rather are pivoted away from the bisecting positions by 8.8(5)° and 9.7(5)°, respectively, towards the NMe_2 group. A similar distortion was found in **5**. Fourthly, the bond angles defined at the ring atoms by their two exocyclic substituents average 109.1(8)°, which is similar to the 108.0(3)° value found in **5**. These angles seem small in view of the relatively high s character ascribed to the hybrid orbitals used by a cyclopropyl ring atom in its exocyclic bonds.[10]

A drawing of **3g** is given in Figure 2. The nearly eclipsed conformation about the B−C(3) bond and its great length,

Table 2. EI mass-spectral data for **2a**−**2i** and **3b**−**4**

	m/*z* (%) [fragment$^+$]
2a	165 (100) [$C_{13}H_9^+$], 74 (43) [$F_2BN(CH_3)_2^+$], 77 (33) [$C_6H_5^+$], 240(31) [$M^+ - C_2F_5$], 91(26) [$C_7H_7^+$], 290(25) [$M^+ - CF_3$], 162(19) [$M^+ - C_2F_5 - C_6H_5$], 359(5) [M^+]
2b	165 (100) [$C_{13}H_9^+$], 91 (15) [$C_7H_7^+$], 74 (12) [$F_2BN(CH_3)_2^+$], 357 (1) [M^+]
2c	134 (100) [$(CH_3)_2NCHC_6H_5^+$], 74 (80) [$F_2BN(CH_3)_2^+$], 42 (77) [CH_3NCH^+], 91 (19) [$C_7H_7^+$], 164 (33) [$M^+ - C_2F_5$], 168 (23) [$C_6H_5BFCFNHCH_3^+$], 77 (17) [$C_6H_5^+$], 214 (15) [$M^+ - CF_3$], 182 (10) [$C_6H_5BFCFN(CH_3)_2^+$], 283 (3) [M^+]
2d	152 (100) [$(CH_3)_2NCHC_6H_4F^+$], 42 (68) [CH_3NCH^+], 74 (60) [$F_2BN(CH_3)_2^+$], 109 (30) [$C_7H_6F^+$], 232 (21) [$M^+ - CF_3$], 182 (15) [$M^+ - C_2F_5$], 301 (3) [M^+]
2e	152 (100) [$(CH_3)_2NCHC_6H_4F^+$], 42 (20) [CH_3NCH^+], 74 (22) [$F_2BN(CH_3)_2^+$], 186 (18) [$FC_6H_4BFCFNHCH_3^+$], 109 (5) [$C_7H_6F^+$], 232 (4) [$M^+ - CF_3$], 182 (4) [$M^+ - C_2F_5$], 301 (2) [M^+]
2f	152 (100) [$(CH_3)_2NCHC_6H_4F^+$], 42 (21) [CH_3NCH^+], 186 (19) [$FC_6H_4BFCFNHCH_3^+$], 74 (18) [$F_2BN(CH_3)_2^+$], 109 (6) [$C_7H_6F^+$], 232 (7) [$M^+ - CF_3$], 182 (4) [$M^+ - C_2F_5$], 301 (3) [M^+]
2g	224 (100) [$(CH_3)_2NCHC_6F_5^+$], 230 (43) [$F_2CCHC_6F_5^+$], 42 (38) [CH_3NCH^+], 258 (29) [$M^+ - C_2F_4 - CH_3$], 74 (27) [$F_2BN(CH_3)_2^+$], 254 (5) [$M^+ - C_2F_5$], 304 (5) [$M^+ - CF_3$]
2h	100 (100) [$(CH_3)_2NCHCH(CH_3)_2^+$], 44 (66) [$(CH_3)_2N^+$], 106 (60) [$M^+ - C_2F_4 - (CH_3)_2CH$], 148 (5) [$F_2BCCH(CH_3)_2N(CH_3)_2^+$]
2i	57 (100) [$(CH_3)_3C^+$], 44 (79) [$(CH_3)_2N^+$], 70 (51) [$(CH_3)_3CCH^+$], 106 (39) [$M^+ - C_2F_4 - (CH_3)_3C$], 114 (21) [$(CH_3)_2NCHC(CH_3)_3^+$], 148 (7) [$F_2BCCH(CH_3)_2N(CH_3)_2^+$], 156 (5) [$M^+ - CF_2 - (CH_3)_3C$], 213 (4) [$M^+ - CF_2$], 263 (2) [$M^+$]
3b	194 (100) [$CH_3NHC_{13}H_8^+$], 209 (76) [$(CH_3)_2NHC_{13}H_8^+$], 211 (64) [$M^+ - C_2F_5 - NH(CH_3)_2$], 165 (46) [$C_{13}H_9^+$], 44 (22) [$(CH_3)_2N^+$], 256 (20) [$M^+ - C_2F_5$], 306 (3) [$M^+ - CF_3$]
3c	42 (100) [CH_3NCH^+], 120 (88) [$CH_3NHCHC_6H_5^+$], 44 (76) [$(CH_3)_2N^+$], 137 (35) [$M^+ - C_2F_5 - NH(CH_3)_2$], 91 (19) [$C_7H_7^+$], 182 (26) [$M^+ - C_2F_5$], 135 (25) [$(CH_3)_2NHCHC_6H_5^+$], 77 (13) [$C_6H_5^+$], 232 (2) [$M^+ - CF_3$]
3d	138 (100) [$CH_3NHCHC_6H_4F^+$], 42 (88) [CH_3NCH^+], 44 (67) [$(CH_3)_2N^+$], 155 (42) [$M^+ - C_2F_5 - NH(CH_3)_2$], 200 (24) [$M^+ - C_2F_5$], 152 (23) [$(CH_3)_2NCHC_6H_4F^+$], 109 (13) [$C_7H_6F^+$], 250 (2) [$M^+ - CF_3$]
3e	138 (100) [$CH_3NHCHC_6H_4F^+$], 44 (66) [$(CH_3)_2N^+$], 42 (45) [CH_3NCH^+], 200 (44) [$M^+ - C_2F_5$], 155 (42) [$M^+ - C_2F_5 - NH(CH_3)_2$], 152 (16) [$(CH_3)_2NCHC_6H_4F^+$], 109 (7) [$C_7H_6F^+$], 250 (3) [$M^+ - CF_3$]
3f	138 (100) [$CH_3NHCHC_6H_4F^+$], 200 (65) [$M^+ - C_2F_5$], 155 (65) [$M^+ - C_2F_5 - NH(CH_3)_2$], 44 (45) [$(CH_3)_2N^+$], 42 (24) [$CH_3NCH^+$], 152 (21) [$(CH_3)_2NCHC_6H_4F^+$], 109 (6) [$C_7H_6F^+$], 250 (6) [$M^+ - CF_3$]
3g	210 (100) [$CH_3NHCHC_6F_5^+$], 44 (86) [$(CH_3)_2N^+$], 272 (77) [$M^+ - C_2F_5$], 225 (55) [$(CH_3)_2NHCHC_6F_5^+$], 227 (34) [$M^+ - C_2F_5 - NH(CH_3)_2$], 42 (30) [$CH_3NCH^+$], 322 (9) [$M^+ - CF_3$]
3h	86 (100) [$CH_3NHCHC_3H_7^+$], 148 (68) [$M^+ - C_2F_5$], 198 (11) [$M^+ - CF_3$]
3i	46 (100) [$(CH_3)_2NH_2^+$], 100 (97) [$CH_3NHCHC_4H_9^+$], 44 (93) [$(CH_3)_2N^+$], 162 (76) [$M^+ - C_2F_5$], 106 (64) [$M^+ - C_2F_5 - (CH_3)_2CCH_2$], 57 (50) [$C_4H_9^+$], 115 (26) [$(CH_3)_2NHCHC_4H_9^+$], 212 (13) [$M^+ - CF_3$]
3j	72 (100) [$CH_3NH_2CHCO^+$], 131 (30) [$(CH_3)_2NHCCH_3CO_2CH_3^+$], 116 (15) [$(CH_3)_2NHCCH_3CO_2^+$], 178 (7) [$M^+ - C_2F_5$], 228 (3) [$M^+ - CF_3$]
3k	72 (100) [$CH_3NH_2CHCO^+$], 116 (43) [$(CH_3)_2NHCCH_3CO_2^+$], 100 (33) [$(CH_3)_2NHCCH_3CO^+$], 192 (24) [$M^+ - C_2F_5$], 145 (15) [$(CH_3)_2NHCCH_3CO_2C_2H_5^+$], 242 (8) [$M^+ - CF_3$]
3l	86 (100) [$(CH_3)_2NHCHCO^+$], 58 (62) [$(CH_3)_2NCH_2^+$], 102 (50) [$(CH_3)_2NHCHCO_2^+$], 164 (38) [$M^+ - C_2F_5$], 117 (35) [$(CH_3)_2NHCHCO_2CH_3^+$], 214 (8) [$M^+ - CF_3$]
3m	86 (100) [$(CH_3)_2NHCHCO^+$], 150 (47) [$M^+ - C_2F_5 - C_4H_8$], 103 (45) [$(CH_3)_2NHCHCO_2H^+$], 57 (26) [$(CH_3)_3C^+$], 58 (14) [$(CH_3)_2NCH_2^+$], 200 (8) [$M^+ - CF_3 - C_4H_8$], 256 (2) [$M^+ - CF_3$], 206 (1) [$M^+ - C_2F_5$]
4	124 (100) [$M^+ - C_2F_5$], 56 (15) [$C_3H_6N^+$], 49 (13) [BF_2^+], 60 (10) [H_3CNCF^+], 108 (6) [$M^+ - C_2F_5 - CH_4$], 174 (1) [$M^+ - CF_3$]

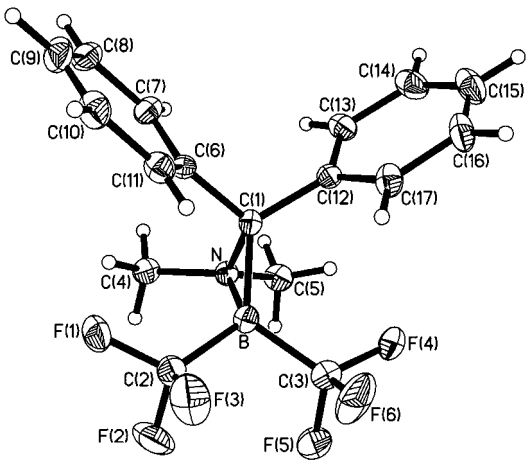


Figure 1. A perspective drawing of **2a**

1.683(4) Å, are reminiscent of the structures reported previously for $B(CF_3)_2(OH)CH(Ph)NH(Bz)(tBu)$ (**6**)[11] and $B(CF_3)_2(OH)CH(SiMe_3)NHMe_2$ (**7**)[3] − the corresponding B−C bond lengths being 1.673(4) and 1.690(4) Å, respectively. Each compound exhibits a synperiplanar O−B−C(3)−N torsion angle − their values of 20.3(5)° and 19.6(5)° in **6** and **7**, respectively, being significantly larger than in **3g**, 11.6(3)°. While the conformation in **6** and **7** is stabilized by moderately strong intramolecular N−H···O hydrogen bonds of 1.88(2) and 1.82(3) Å, respectively, the corresponding distance in **3g**, 2.41(3) Å, is too long to be bonding. Here the nitrogen atom donates its proton to an oxygen atom of an inversion-related molecule, 2.03(3) Å; thus, centrosymmetric, hydrogen-bonded dimers are formed in the solid state. Perhaps the absence of intramolecular hydrogen bonding in **3g** accounts for its O−B−C(3) and B−C(3)−N angles [110.2(2)° and 111.4(2)°, respectively] being on the average 5(1)° larger than the analogous angles of **6** and **7**.

Because hindered rotation was detected by NMR spectroscopy for the C_6F_5 group, we note that the aryl group in **3g** is oriented roughly parallel to the C(3)−H(3) bond − the H(3)−C(3)−C(6)−C(11) torsion angle being 17(2)°. A similar orientation was found for the corresponding phenyl substituent of **6**. In **3g** the aryl group protrudes into a cavity

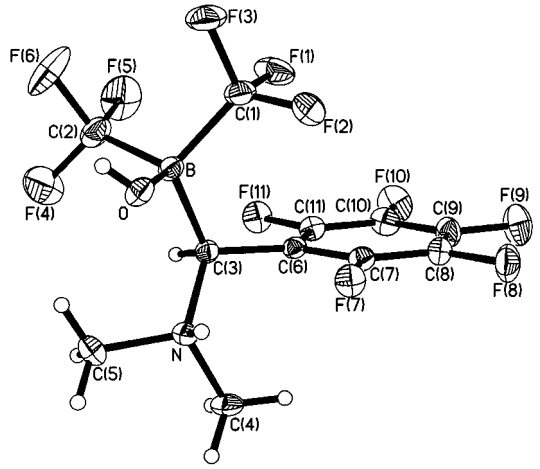
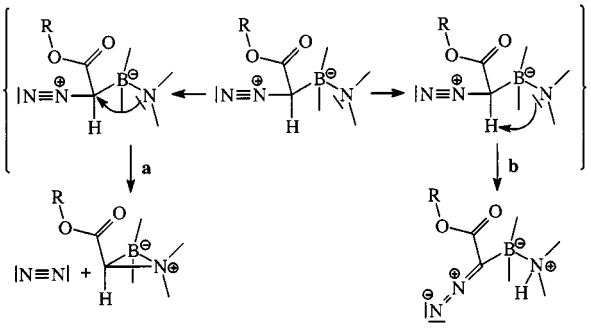


Figure. 2. A perspective drawing of **3g**

in which the CH_3 group of C(4) and the CF_3 group of C(1) are on opposites sides of the ring plane.

Discussion

The divergent behavior of the three diazoacetic acid esters $HC(N_2)COOR$ (R = *t*Bu, Et and Me) is not fully understood. The acetic acid esters H_3CCOOR with R = *t*Bu, Et undergo an ene-type reaction with **1** regardless of their substituent R. Therefore we speculate that the mechanism which leads to ene-type products of acetic acid esters and the diazoacetic acid ethyl ester are different. The reaction of all diazomethane derivatives with **1** is obviously initiated by a nucleophilic attack of boron at the diazo carbon atom (Scheme 4). The transient complex thus formed has two ways to gain stabilization. In pathway **a** the nitrogen lone pair attacks the diazomethane carbon atom, dinitrogen is eliminated and the three-membered ring is fused. In pathway **b** the lone pair abstracts a proton bonded to the diazomethane carbon atom − the diazo group being preserved.



Scheme 4. Formation of azoniaboratecyclopropanes and ene-type reaction products with **1** and diazomethane derivatives

A small conformational change in the transition complex, as determined by the N−B−C−H torsional angle, is presumably responsible for the formation of azoniaboratacyclopropanes (route **a**) or ene-products (route **b**). The conformation about the B−C bond should be affected by the varying shape of the groups R [R = Me, *t*Bu (C_3 symmetry) and R = Et (C_s symmetry)], and the conformation governs the distances between the lone pair, the carbon atom and the hydrogen atom and thus the reaction pathway. Route **b** is, however, also dependent on the acidity of the abstracted proton. Therefore this route is only observed for diazocarbonyl derivatives.

The failure to synthesize the three-membered ring *cyclo*-$(F_3C)_2B-CF_2-NMe_2$ animated us to compare the difference in its calculated energy and that of **4** to the analogous difference of *cyclo*-$(F_3C)_2B-CH_2-NMe_2$ versus $(F_3C)_2BH-CH=NMe_2$. According to semi-empirical AM1 calculations the energy of *cyclo*-$(F_3C)_2B-CH_2-NMe_2$ is ca. 2 kcal/mol lower than that of $(F_3C)_2BH-CH=NMe_2$ while **4** is ca. 30 kcal/mol more stable than *cyclo*-$(F_3C)_2B-CF_2-NMe_2$

Experimental Section

General: NMR: Bruker ARX 400 (400 MHz, 100.6 MHz and 376.5 MHz, for ^1H, ^{13}C and ^{19}F respectively), Bruker AC 250 (79.8 MHz for ^{11}B). [D_3]Acetonitrile as solvent and internal standard (^1H: $\delta_H = 1.95$; ^{13}C: $\delta_C = 1.30$), $CDCl_3$ as solvent and internal standard (^1H: $\delta_H = 7.27$; ^{13}C: $\delta_C = 77.0$), [D_6]acetone as solvent and internal standard (^1H: $\delta_H = 2.05$; ^{13}C: $\delta_C = 29.8$), CD_2Cl_2 as solvent and internal standard (^1H: $\delta_H = 5.35$; ^{13}C: $\delta_C = 53.8$), ^{19}F external standard $CFCl_3$, ^{11}B external standard $BF_3 \cdot OEt_2$. − IR: Bruker IFS 25. − MS: Varian MAT 311 (70 eV).

X-ray Structure Determinations: Crystals of **2a** and **3g** were grown from solutions in $CHCl_3$ and acetone/H_2O, respectively. While crystals of **2a** were sealed in glass capillaries under nitrogen, those of **3g** were glued to glass fibers. The structures were solved and refined using absorption-corrected X-ray data with the SHELXTL program package.[12] While the H(N) and H(O) atoms of **3g** were refined freely, the positions of all other hydrogen atoms were idealized. Crystal data are summarized in Table 3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102694 for **2a** and -102695 for **3g**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

1,1-Dimethyl-3,3-diphenyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2a), 3-Fluorenyl-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2b), 1,1-Dimethyl-3-phenyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2c), 3-(4-Fluorophenyl)-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2d), 3-(3-Fluorophenyl)-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2e), 3-(2-Fluorophenyl)-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2f), 1,1-Dimethyl-3-(pentafluorophenyl)-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2g), 3-Isopropyl-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2h), 3-*tert*-Butyl-1,1-dimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2i), 3-(Methoxycarbonyl)-1,1,3-trimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2j), 3-(Ethoxycarbonyl)-1,1,3-trimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-boratacyclopropane (2k). − General Procedure: 10×10^{-3} mol of the respective neat diazomethane (Scheme 2) and 10−15 ml of pentane (stored over P_4O_{10}) were condensed at −196°C into a U-shaped reaction vessel connected to a vacuum line. By warming the vessel, pentane and the diazomethane were mixed. The vessel was cooled

Table 3. Crystal data and structure refinement

Compound	**2a**	**3g**
Formula	$C_{17}H_{16}BF_6N$	$C_{11}H_9BF_{11}NO$
M_r	359.12	391.00
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a [Å]	7.592(2)	8.409(1)
b [Å]	12.836(3)	14.179(2)
c [Å]	17.539 (4)	12.417(2)
β [°]	90	91.52(1)
Z	4	4
D(calcd.) [g cm^{-3}]	1.396	1.755
T [K]	297(2)	294(2)
Diffractometer	Siemens AED 1	Siemens P3
λ [Å]	0.71073	1.54184
Monochromation	Zr filter	graphite
θ range [°]	2.3−25.0	4.7−69.0
Quadrants	$h, \pm k, \pm l$	$h, k, \pm l$
Reflections collected	3475	2879
Unique	1738	2750
Observed [$I > 2\sigma(I)$]	1028	2184
μ (λ) [mm^{-1}]	0.127	1.890
Crystal size [mm]	0.46 × 0.24 × 0.13	0.36 × 0.34 × 0.11
Transmission	0.971−0.984	0.606−0.825
Parameters	232	243
R_F (observed)	0.044	0.054
wR_F^2 (all data)	0.085	0.158
Final diff. density [e Å^{-3}]	0.15 to −0.16	0.53 to −0.40

again to −196°C and 2 g (11 × 10^{-3} mol) of $(F_3C)_2BNMe_2$ and ca 10 ml of pentane were condensed onto the diazomethane/pentane mixture. The reaction vessel was gassed with dry nitrogen and allowed to warm to room temperature under stirring. After 10 min at 20°C, all volatile material was removed in vacuo. According to NMR spectra the reaction was quantitative and the products were analytically pure.

3-Fluorenyl-5,5,5-trifluoro-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3b), 5,5,5-Trifluoro-4-hydroxy-2-methyl-3-phenyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3c), 5,5,5-Trifluoro-3-(4-fluorophenyl)-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3d), 5,5,5-Trifluoro-3-(3-fluorophenyl)-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3e), 5,5,5-Trifluoro-3-(2-fluorophenyl)-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3f), 5,5,5-Trifluoro-4-hydroxy-2-methyl-3-(pentafluorophenyl)-4-(trifluoromethyl)-2-azonia-4-boratapentane (3g), 5,5,5-Trifluoro-4-hydroxy-3-isopropyl-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3h), 3-*tert*-Butyl-5,5,5-trifluoro-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3i), 5,5,5-Trifluoro-4-hydroxy-3-(methoxycarbonyl)-2,3-dimethyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3j), 3-(Ethoxycarbonyl)-5,5,5-trifluoro-4-hydroxy-2,3-dimethyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3k), 5,5,5-Trifluoro-4-hydroxy-3-(methoxycarbonyl)-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3l), 3-(*tert*-Butoxycarbonyl)-5,5,5-trifluoro-4-hydroxy-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapentane (3m). − General Procedure: A solution (3 × 10^{-3} mol) of the corresponding azoniaboratacyclopropane in 10 ml of CH_2Cl_2 was stirred with 20 × 10^{-3} mol of H_2O for 12 h at ambient temperature. After removal of the solvent and the water in vacuo, pure **3b**−**3m** were obtained in quantitative yield.

3b: M.p. 160°C. − IR: $\tilde{\nu}$ = 3636 cm^{-1} (OH), 3270 (NH), 1078 (CF).

3c: M.p. 96°C. − IR: $\tilde{\nu}$ = 3638 cm^{-1} (OH), 3278 (NH), 1107, 1083 (CF).

Table 4. Elemental analyses of **2a**−**2c** and **3b**−**3m**

Compound	Formula	found/(calcd.)		
		C	H	N
2a	$C_{17}H_{16}BF_6N$	56.5/(56.86)	4.4/(4.49)	3.9/(3.90)
2b	$C_{17}H_{14}BF_6N$	55.3/(57.18)	4.1/(3.95)	4.0/(3.92)
2c	$C_{11}H_{12}BF_6N$	46.0/(46.68)	4.3/(4.27)	4.7/(4.95)
3b	$C_{17}H_{16}BF_6NO$	54.2/(54.43)	4.6/(4.30)	3.7/(3.73)
3c	$C_{11}H_{14}BF_6NO$	43.8/(43.89)	4.6/(4.69)	4.4/(4.65)
3d	$C_{11}H_{13}BF_7NO$	41.4/(41.41)	4.3/(4.11)	4.6/(4.39)
3e	$C_{11}H_{13}BF_7NO$	40.8/(41.41)	4.3/(4.11)	4.5/(4.39)
3f	$C_{11}H_{13}BF_7NO$	41.1/(41.41)	4.0/(4.11)	4.5/(4.39)
3g	$C_{11}H_9BF_{11}NO$	33.4/(33.79)	2.3/(2.32)	3.2/(3.58)
3h	$C_8H_{16}BF_6NO$	35.0/(35.99)	5.2/(6.04)	5.6/(5.25)
3i	$C_9H_{18}BF_6NO$	36.9/(38.46)	6.0/(6.46)	5.5/(4.98)
3j	$C_8H_{14}BF_6NO_3$	32.4/(32.35)	4.8/(4.75)	4.1/(4.72)
3k	$C_9H_{16}BF_6NO_3$	34.0/(34.76)	5.0/(5.19)	4.7/(4.50)
3l	$C_7H_{12}BF_6NO_3$	29.6/(29.71)	4.3/(4.27)	5.3/(4.95)
3m	$C_{10}H_{18}BF_6NO_3$	36.8/(36.95)	5.4/(5.58)	3.6/(4.31)

3d: M.p. 100°C. − IR: $\tilde{\nu}$ = 3663 cm^{-1} (OH), 3262 (NH), 1092 (CF).

3e: M.p. 104°C. − IR: $\tilde{\nu}$ = 3643 cm^{-1} (OH), 3270 (NH), 1086 (CF).

3f: M.p. 102°C. − IR: $\tilde{\nu}$ = 3646 cm^{-1} (OH), 3272 (NH), 1086, 1025 (CF).

3g: M.p. 110°C. − IR: $\tilde{\nu}$ = 3661 cm^{-1} (OH), 3257 (NH), 1091 (CF).

3h: M.p. 60°C. − IR: $\tilde{\nu}$ = 3671 cm^{-1} (OH), 3277 (NH), 1074, 1021 (CF).

3i: M.p. 92°C. − IR: $\tilde{\nu}$ = 3663 cm^{-1} (OH), 3269 (NH), 1094, 1074 (CF).

3j: M.p. 120°C. − IR: $\tilde{\nu}$ = 3164 cm^{-1} (NH), 1708 (C=O), 1086 (CF).

3k: M.p. 106°C. − IR: $\tilde{\nu}$ = 3161 cm^{-1} (NH), 1705 (C=O), 1106, 1081 (CF).

3l: M.p. 124°C. − IR: $\tilde{\nu}$ = 3670 cm^{-1} (OH), 3082 (NH), 1716 (C=O), 1086 (CF).

3m: M.p. 140°C. − IR: $\tilde{\nu}$ = 3435 cm^{-1} (OH), 3254 (NH), 1688 (C=O), 1088 (CF).

3,4,5,5,5-Pentafluoro-2-methyl-4-(trifluoromethyl)-2-azonia-4-boratapent-2-ene (4): 1 g (6.5 × 10^{-3} mol) of F_3CSiF_3 and 1.25 g (6.5 × 10^{-3} mol) of **1** were condensed at −196°C into an ampoule fitted with a PTFE valve. The ampoule was slowly warmed to room temperature and all volatile material was removed in vacuo. The brown residue was crystallized from a $CH_2Cl_2/CHCl_3$ mixture. Yield 89%; decomp. ca. 40°C. − IR: $\tilde{\nu}$ = 1684 cm^{-1} (C=N), 1112, 1081, 1051 (CF). − For elemental analyses see Table 4.

Acknowledgments

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

[1] G. Pawelke, H. Bürger, *Appl. Organomet. Chem.* **1996**, *10*, 147−174.
[2] A. Ansorge, D. J. Brauer, H. Bürger, T. Hagen, G. Pawelke, *Angew. Chem.* **1993**, *105*, 429−430; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 384−385.

[3] A. Ansorge, D. J. Brauer, H. Bürger, T. Hagen, G. Pawelke, *J. Organomet. Chem.* **1994**, *467*, 1−11.
[4] H. Beckers, H. Bürger, *J. Organomet. Chem.* **1990**, *385*, 207−219.
[5] D. J. Brauer, H. Bürger, T. Dittmar, G. Pawelke, *J. Organomet. Chem.* **1996**, *524*, 225−235.
[6] J. W. Lauber, J. A. Ibers, *J. Amer. Chem. Soc.* **1975**, *97*, 561−567.
[7] D. J. Brauer, S. Buchheim-Spiegel, H. Bürger, R. Gielen, G. Pawelke, J. Rothe, *Organometallics* **1997**, *16*, 5321−5330.
[8] D. J. Brauer, H. Bürger, G. Pawelke, J. Rothe, *J. Organomet. Chem.* **1995**, *522*, 129−136.
[9] A. Ansorge, D. J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke, W. Weuter, *J. Organomet. Chem.* **1990**, *396*, 253−267.
[10] F. H. Allen, *Acta Crystallogr.* **1981**, *B37*, 890−900.
[11] A. Ansorge, D. J. Brauer, H. Bürger, F. Dörrenbach, B. Krumm, G. Pawelke, *Z. Naturforsch.* **1992**, *47b*, 772−782.
[12] G. M. Sheldrick, *SHELXTL Version 5.03*, Siemens Industrial Automation, Inc., Madison, WI, **1994**.

Received September 21, 1998
[I98322]