Journal of Organometallic Chemistry, 396 (1990) 253–267
Elsevier Sequoia S.A., Lausanne
JOM 21014

[2 + 4] Cycloaddition reactions of dialkylaminobis(trifluoromethyl)boranes with 1,3-dienes, β-unsaturated carbonyl compounds and methyl methacrylate. Crystal structures of $(CF_3)_2\overline{BNR_2CH_2C(Me)C(Me)C}H_2$, R = Me and Et, and $(CF_3)_2\overline{BNEt_2CH_2CHC(Me)O}$

A. Ansorge, D.J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter

Anorganische Chemie, Fachbereich 9, Universität-Gesamthochschule, D-5600 Wuppertal (F.R.G.)

(Received April 3rd, 1990)

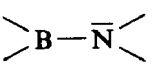
Abstract

Hitherto unknown [2 + 4] addition reactions of aminoboranes were observed when dialkylaminobis(trifluoromethyl)boranes $(CF_3)_2BNR_2$, R = Me and Et, were treated with a variety of 1,3-unsaturated compounds of the type $X{=}CR^3CR^2{=}CHR^1$, where X = CH_2 or O. The cycloaddition products of the general formula $(CF_3)_2\overline{BNR_2CHR^1CR^2{=}CR^3X}$ were obtained in high yields. Ring closure was sterically hindered when the enone was $O{=}C(Me)CH{=}CMe_2$, the B-alkylation product $(CF_3)_2B(NHMe_2)CH_2C(O)CH{=}CMe_2$ being formed instead by an ene reaction. Twelve novel boracyclohexene derivatives were isolated and characterized by multinuclear NMR spectroscopy and by mass spectrometry, and IR and Raman spectroscopy. The crystal structures of the compounds $(CF_3)_2\overline{BNR_2CH_2\text{-}CMe{=}CMeC}H_2$, R = Me and Et, and $(CF_3)_2\overline{BNEt_2CH_2CHCMeO}$ have been determined by X-ray diffraction studies. They show that the B–N and B–CF_3 bonds are somewhat longer than those in acyclic amine adducts of bis(trifluoromethyl)boranes. Furthermore, evidence is presented for steric congestion of the ring substituents.

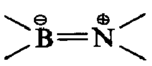
Introduction

The formal analogy between the isosteric BN and CC bonds in e.g., aminoboranes (borazenes) $R'_2B{=}NR_2$ and alkenes $R''_2C{=}CR_2$ has long acted as a stimulus to synthetic and theoretical and structural investigations. Although, for reasons to be discussed, aminoboranes do not truly resemble alkenes in reactivity, structure arguments favour the presence of strong alkene-like double bond character (**B**).

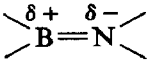
0022-328X/90/$03.50



A



B

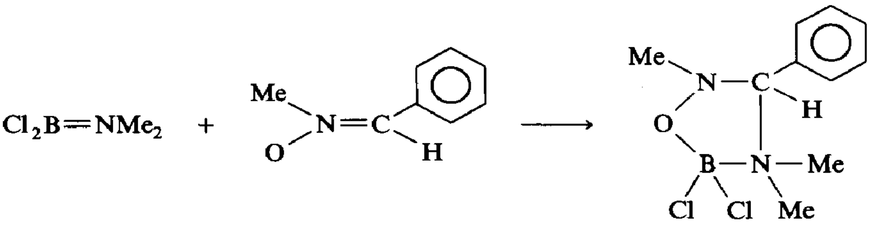


C

The question of whether this BN bond can really have full double bond character seems to be not fully settled. While the average BN bond length of 1.41 Å in various aminoboranes has been judged to refer to a BN double bond by comparison with typical single bond lengths of 1.58 Å [1], the 0.27 Å bond shortening from 1.66 Å in H_3BNH_3 [2] to 1.391(2) Å in H_2BNH_2 [3] has been suggested to arise mainly from increase in $(N \rightarrow B)\pi$ bonding [4]. An analogous shortening, 0.22 Å, is observed in $(CF_3)_2BN(i\text{-}Pr)_2$ (**D**) (1.37 Å [5]) compared to $(CF_3)_3B \cdot NHEt_2$ and $(CF_3)_3B \cdot NH_2Et$ (1.59 Å [6]). The planarity of the $>B{=}N<$ skeleton in H_2BNH_2 [3] and **D** [5], and on the basis of an electron diffraction investigation also strongly favoured for $(CF_3)_2BNMe_2$ [7], is not attributable to any steric requirements, and so lends additional support to the assumption of alkene-like BN bonds in aminoboranes in general and bis(trifluoromethyl)boron derivatives in particular: Theoretical calculations suggest, however, that the decrease of the π-bond energy when the R'_2B and NR_2 groups are twisted to orthogonality is only half that for analogous alkenes [4].

On the other hand, the BN bond is quite polar, with a $\delta+$ charge on boron and a $\delta-$ charge on nitrogen [1,8], and so formula **C** is more appropriate than **B**.

The charge distribution depicted as **B** favours polar reactions. On the other hand, [2 + 4] cycloaddition reactions of alkenes are commonly assumed to proceed by a concerted multicenter mechanism. It is therefore not surprising that so far aminoboranes have not been found to act as ene component in [2 + 2], [2 + 3] or [2 + 4] cycloaddition reactions. Furthermore activation of aminoboranes by placing halogen substituents on boron results in an enhanced tendency towards cyclodimerization. Moreover, the B–halogen bonds are themselves very reactive, the good leaving group character of halides facilitating nucleophilic attack at boron. It is nevertheless surprising that only one example of a [2 + 3] cycloaddition reaction yielding a stable addition product has been reported; in this, an aminoborane reacts with an aldimine-*N*-oxide according to eq. (1) [9].



(1)

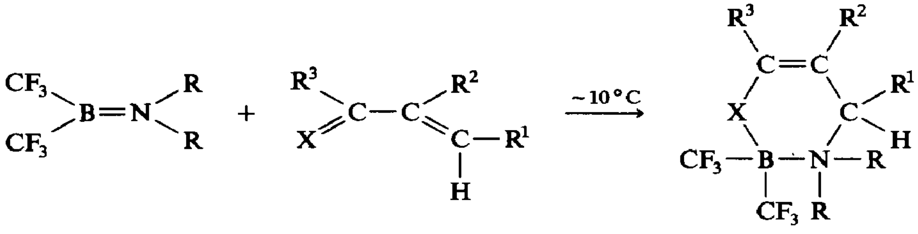
The effective strengthening of the BN bond by CF_3 substituents, as indicated by short bond length, the resistance to nucleophilic displacement of the CF_3 groups, and the absence of any tendency to cyclodimerize makes the dialkylaminobis(trifluoromethyl)boranes $(CF_3)_2BNR_2$, R = Me [10], Et and i-Pr [5] particularly suited for addition reactions. In a preceding study [5] we investigated their reactions with HF, HCl, HBr and H_2O. Now we report on their use as ene components in a variety of [2 + 4] cycloadditions to yield novel six-membered boraheterocycles, and we discuss the limitations of this versatile synthesis.

[2 + 4] Cycloaddition Reactions

The dialkylaminobis(trifluoromethyl)boranes I and II react at or below room

$(CF_3)_2BNMe_2$ (I) $(CF_3)_2BNEt_2$ (II)

temperature according to eq. 2 with a variety of 1,3-unsaturated systems, viz., substituted dienes $R^1CH{=}C(R^2)C(R^3){=}CH_2$, 1-buten-3-one $CH_3C(O)CH{=}CH_2$, methyl methacrylate $CH_3OC(O)C(CH_3){=}CH_2$, 2-methyl-2-butenal $CH_3CH{=}C(CH_3)CHO$, 1-methoxy-1-buten-3-one $CH_3OCH{=}CHC(O)CH_3$ and 1-acetylcyclohexene $CH_3C(O)C{=}CHCH_2CH_2CH_2CH_2$, to yield the novel six-membered boraheterocyclic compounds III–XIII (eq. 2).



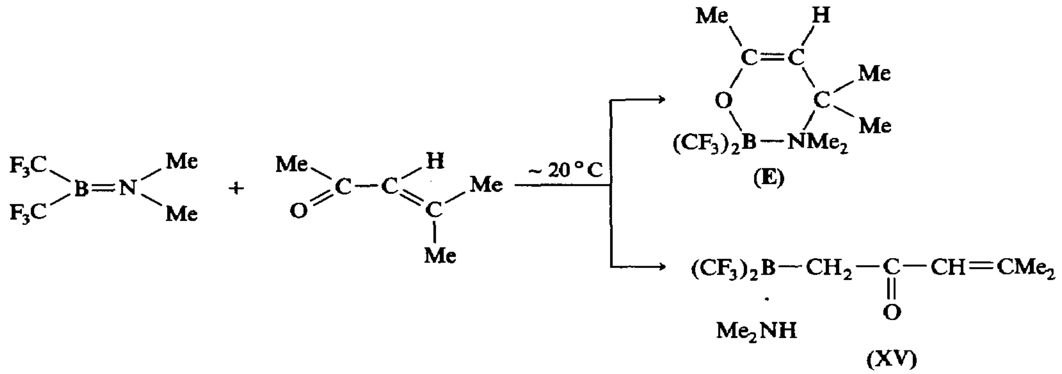
(III–XIII)

(2)

X	R	R^1	R^2	R^3		yield %
CH_2	Me	H	Me	Me	(III)	85
	Et	H	Me	Me	(IV)	95
	Me	H	H	Me	(V)	92
	Et	H	H	Me	(VI)	70
	Me	Me	H	Me	(VII)	95
O	Me	H	H	Me	(VIII)	82
	Et	H	H	Me	(IX)	45
	Me	H	Me	OMe	(X)	83
	Me	Me	Me	H	(XI)	29
	Me	OMe	H	Me	(XII)	60
	Me	$(CH_2)_4$		Me	(XIII)	93

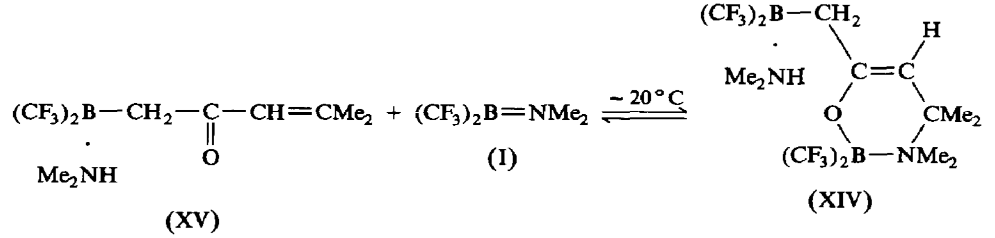
Steric hindrance by bulky substituents limits the scope of this cycloaddition reaction. Thus, whereas I reacts readily with e.g. acetylcyclohexene, no such cycloaddition was observed with the diethylaminoborane II. On the other hand, electrophilic attack by the B atom requires an unsubstituted terminal $>C{=}CH_2$ entity, such as is present in 1-alkenes. In experiments with 2,4-hexadiene, 1,3-cyclohexadiene, or cyclopentadiene as the diene component, no cycloadducts were formed.

Ring closure by formation of an N–C bond is similarly prevented, or at least hindered, if the carbon atom attacked by the nucleophilic nitrogen carries more than one alkyl substituent. Thus, the reaction of I with 2-methyl-2-penten-4-one (eq. 3) proceeds in a completely different way; B-alkylation giving XV, (in ca. 10% yield) rather than the cycloadduct E. Even in the presence of an excess of the pentenone,



(3)

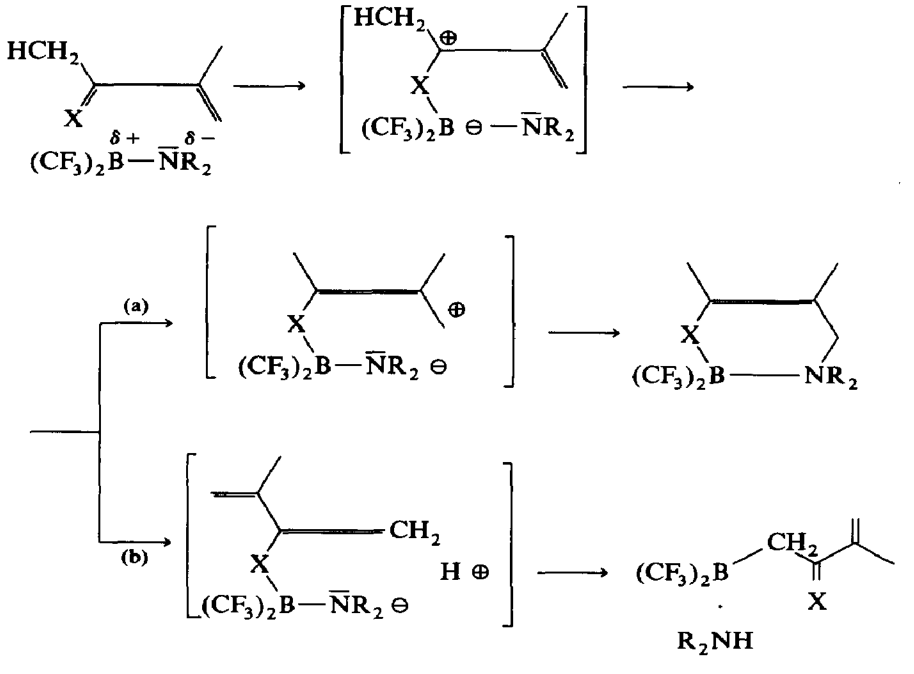
XV adds to further I to give XIV in moderate yield, eq. 4. XIV, which was identified from its ^{1}H, ^{19}F, ^{13}C NMR spectra, could not be isolated but dissociated into XV and I in a retro-Diels–Alder type reaction during attempted purification by sublimation in vacuo. Thus reaction 4 is presumably an equilibrium, which reveals the rôle played by substituents at the electrophilic center of the diene or enone.



(4)

The above-mentioned B-alkylation of I is not restricted to the reaction with 2-methyl-2-penten-4-one but takes place quite generally with various other types of unsaturated species, e.g. alkenes, ketones, nitriles, alkynes, etc., as will be described in a later publication.

The [2 + 4] cycloaddition and the B-alkylation are initiated by the same electro-



(5a)

(5b)

philic attack by the B atom on the double bond. More negative charge develops on the nitrogen atom, while the carbocation can stabilize itself either by formation of the carbenium ion required for the subsequent ring closure (a) or by proton transfer to the NR_2 group followed by a rearrangement to form the B-alkylation product (b).

Yields of isolated cycloaddition products are generally high. The addition reactions themselves proceed almost quantitatively, but there is some loss of material during work-up by sublimation in vacuo owing to the limited thermal stability of the product. Compounds IX and XI were obtained only in moderate yields.

Properties and spectra

All the novel trifluoromethylboron derivatives III–XV are air-stable volatile solids, those containing a B–O bond being sensitive to moisture. Melting points are listed in Table 1.

Valuable information related to their constitution and structure can be obtained from their ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra. The relevant chemical shifts δ are listed in Table 1. In general, the ^1H signals are too broad to provide accurate information on (small) $H \cdots H$ couplings, and such data have been omitted from Table 1. As expected, VII, XI, XII and XIII exhibit two resonances for the magnetically non-equivalent NCH_3 and BCF_3 groups. The ^{19}F and ^{11}B chemical shifts are almost invariant; the signals are quite broad, $^{19}F^{11}B$ coupling being just detectable in some cases.

More significant information comes from the ^{13}C NMR spectra, which unambiguously confirm the proposed structures. No resonances of the CF_3-carbon atoms were detected. A coupling constant $^4J(CF) \simeq 2$ Hz is normally observed for carbon atoms linked to a $NBCF_3$ fragment [6].

EI mass spectra of the novel cycloadducts were recorded and the main peaks are reported in the Experimental section. Generally the intensity of the M^+ peak is $< 10\%$ of the base peak, which for III–VII is that for the diene component formed by a retro-Diels–Alder reaction. The fragmentation of the molecular ion M^+ usually starts with elimination of CF_3 and/or CF_2 with generation of the characteristic fragments $[M - CF_3]^+$ and $[M - C_2F_5]^+$, which are the base peaks for VIII, IX and XIII. The heterocycles containing a BO bond specifically form the fragment $[FB(O)NR_2]^+$ (R = Me, Et), which is the base peak in the case of XI.

The vibrational (IR and Raman) spectra reported in some detail in the Experimental section are rather complex, and firm assignments are difficult to make, but they do not conflict with the proposed structures and confirm the presence of particular fragments, e.g. CF_3 groups, and N–H (XIV, XV), C=O (XV), and C=C bonds.

Discussion

The reported [2 + 4] cycloaddition (and similarly the B-alkylation) reactions of the bis(trifluoromethyl)boron derivatives I and II are novel for aminoboranes. They are the result of the strong electrophilic character that the B atom possesses in spite of the extensive electron donation from the nitrogen atom that is reflected by the shortness and strength of the BN bond, which, owing to the polarity of the BN bond is insufficient to satisfy the electron demand of the B atom. In contrast to the situation with aminoboron halides, this demand cannot be suppressed by the

Table 1. Physical properties and NMR data for III–XV (δ in ppm) [a].

	III	VI	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
M.p. (°C)	87	70	75	35	69	83	54	58	76	43	107	...	78
^{1}H													
$\delta(\mathrm{NC}H_3)$	2.85		2.83		2.57 2.89	2.84		2.85	2.63 2.87	2.65 2.83	2.66 2.85	2.74 2.82	2.78
$\delta(\mathrm{CH_2C}H_3)$		1.26		1.23			1.34						
$\delta(\mathrm{C}H_2\mathrm{CH_3})$		3.22 3.37		3.22 3.35			3.26 3.35						
$\delta(\mathrm{OC}H_3)$								3.62		3.55			
$\delta(\mathrm{CC}H_3)$					1.29				1.33			1.43	
$\delta(\mathrm{C{=}CC}H_3)$	1.81	1.77	1.59 1.74	1.60 1.71	1.78	1.82	1.84	1.51	1.53	1.80	1.83		1.91 2.10
$\delta(\mathrm{NC}H_x)$	3.50	3.49	3.38	3.37	4.08	3.51	3.54	3.44	4.18	4.37	3.69		
$\delta(\mathrm{BC}H_2)$	1.31	1.33	1.33	1.34	1.27							1.55	1.97
$\delta(\mathrm{C{=}C}H)$	5.14	5.15			4.93	4.35	4.36		6.31	4.94		4.54	6.19
$\delta(\mathrm{NH})$												6.2	6.77
^{19}F													
$\delta(\mathrm{C}F_3)$	−61.7	−60.7	−61.6	−59.7	−61.1 −61.4	−66.3	−64.9	−65.8	−64.8 −65.6	−65.0 −65.9	−64.0 −65.7	−63.9 −64.2	−63.8
^{11}B													
$\delta(B)$	−7.5	−6.7	−7.8	−6.5	−7.1	−3.4	−3.1	−3.3	−3.6	−3.1	−3.3	−1.6 −8.1	−8.1
^{13}C													
$\delta(\mathrm{NCH_3})$	49.9		50.1		40.3 45.8	48.7		48.7	40.3 44.4	39.2 43.1	41.9 44.5	39.6 43.6	39.6
$\delta(\mathrm{CH_2}C\mathrm{H_3})$		9.4		9.4			9.1						
$\delta(C\mathrm{H_2CH_3})$		51.4		51.6			51.9						
$\delta(\mathrm{O}C\mathrm{H_3})$								54.5		59.1			
$\delta(\mathrm{C}C\mathrm{H_3})$					13.2				10.2			23.6	
$\delta(\mathrm{C{=}C}C\mathrm{H}_{3(2)})$	25.5	25.4	16.9 20.9	17.0 21.0	25.4	20.8	20.8	11.8	14.8	20.5	17.2 (27.8)		
$\delta(\mathrm{B}C\mathrm{H_2})$	17.6	18.9	19.2	21.4	18.4							20.0	30.5
$\delta(\mathrm{C}C\mathrm{H_2C})$											25 ± 0.1		
$\delta(\mathrm{N}C\mathrm{H}_x)$	63.7	52.6	68.2	57.5	62.7	61.3	51.4	65.4	64.6	94.0	68.7	68.1	
$\delta(C{=}C)$	112.3 138.5	112.6 140.1	116.5 129.7	116.9 131.4	119.4 139.5	88.2 151.4	89.3 152.5	73.5 149.5	105.1 138.2	91.9 154.1	104.2 142.9	103.4 155.7	126.1 156.6
$\delta(C{=}\mathrm{O})$													208.6

[a] In $CDCl_3$. ^{1}H: 250.13 MHz, internal standard $CHCl_3$ = 7.27 ppm. ^{19}F: 84.67 MHz, internal standard $CFCl_3$. ^{13}C: 62.90 MHz, internal standard $CDCl_3$ = 77.0 ppm. ^{11}B: 25.52 MHz, external standard $F_3B\cdot OEt_2$.

electron-withdrawing CF_3 groups, whose inductive effects are, however, responsible both for the strength of the BN bond in I and II and the stability of the cycloadducts formally involving a dative BN single bond. In trialkylborane-amine complexes such bonds are apparently weaker, thermal cleavage occurring with some ease.

The aminoborane I is significantly more reactive than II. The difference in reactivity is evident , for example, from the failure of II to react with acetylcyclohexene, with which I forms XIII in almost quantitative yield.

The behaviour of I and II resembles more that of iminoboranes, RB≡NR′, than that of other aminoboranes, although the iminoboranes prefer [2 + 2] (e.g., cyclodimerization) and [2 + 3] addition [1] rather than the [2 + 4] Diels–Alder-type reactions described in the present study.

[2 + 2] Cycloaddition of I or II with dienes has never been observed. Such a reaction, occurring along with formation of [2 + 4] cycloadducts and products arising from an intermolecular ene reaction, has, however, been reported for the reaction of silenes $(Me_3Si)_2Si{=}C(R)OSiMe_3$ with 1,3-dienes [11]. In contrast, donor-stabilized iminosilanes, $Me_2Si{=}NSi(t\text{-}Bu)_3 \cdot D$ (D = donor) react with dienes to give exclusively ene reaction products and [2 + 2] and [2 + 3] cycloadducts, no [2 + 4] cycloaddition being observed [12].

Crystallographic structure determination on III, IV and IX

Crystals of III were grown from an ethanol solution and those of IV and IX by sublimation. They were mounted in glass capillaries under argon. Lattice constants (Table 2) and intensity data were measured at 24 °C with a Siemens AED 1 diffractometer employing Zr-filtered Mo-K_α radiation (0.71073 Å). Reflections were scanned by the θ–2θ technique, and the intensities were corrected for the fluctuations of the three hourly monitored standard reflections. The structures were solved by direct methods and refined by full-matrix least squares techniques. Dispersion-corrected Hartree–Fock scattering factors [13] were used for all atoms except hydrogen, for which those of Steward, Davidson and Simpson were employed. Hydrogen atoms were placed in idealized positions (C–H = 0.95 Å) and assigned group isotropic temperature factors. Rotational disorder was found for the C(7) and C(8) methyl groups in III. Nonhydrogen atoms were refined anisotropically – the coordinates obtained at convergence being given in Tables 3, 4 and 5. The numbering schemes are defined by the ORTEP drawings shown in Figs. 1, 2 and 3. The program SHELX-76 [14] was used for structure solution and refinement as well as absorption corrections. No extinction correction was necessary [15*]. Important bond distances and angles are listed in Table 6.

Description of the crystal structures

Compounds III, IV and IX crystallize as discrete monomeric molecules, each possessing a six-membered chelate ring. Each ring exhibits an essentially planar four-atom fragment (C(3), C(4), C(5), C(6) in III and IV and O, C(3), C(4), C(5) in IX), which is consistent with the double bond between the second and third atoms.

---

* Reference number with asterisk indicates a note in the list of references.

Table 2

Crystallographic data for III, IV and IX

	III	IV	IX
Formula	$C_{10}H_{16}BF_6N$	$C_{12}H_{20}BF_6N$	$C_{10}H_{16}BF_6NO$
MW	275.04	303.10	291.04
Space group	$P\bar{1}$ (No.2)	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)
a, Å	7.401(1)	7.784(2)	8.393(2)
b, Å	7.4278(9)	13.476(3)	12.771(4)
c, Å	13.292(2)	14.185(3)	12.569(4)
α, deg	92.40(1)	90	90
β, deg	98.363(7)	101.45(2)	94.13(3)
γ, deg	116.843(8)	90	90
V, Å^3	640.2(4)	1458.4(6)	1343.7(7)
Z	2	4	4
ρ_{calc}, g cm^{-3}	1.427	1.380	1.439
Measured reflections	5202	2956	2590
Unique reflections	3725	2570	2355
Observed ($F_o \geq 4\sigma(F_o)$)	2506	1426	1000
Monitor correction	0.983–1.009	0.992–1.003	0.955–1.179
μ, cm^{-1}	1.4	1.2	1.3
Transmission coefficients	0.917–0.989	0.933–0.989	
R (F_o)	0.074	0.084	0.088
R_w (F_o)	0.112	0.099	0.109
Parameters	177	195	182
ρ(e/Å^3) [a]	+0.51/−0.36	+0.38/−0.27	+0.39/−0.28

[a] Density range in final difference Fourier map.

Table 3

Positional and equivalent isotropic temperature factors [a] for III

Atom	x	y	z	U
B	0.1441(3)	0.3499(4)	0.2244(2)	0.048(1)
N	−0.0960(3)	0.1831(3)	0.1907(1)	0.0492(9)
C(1)	0.2852(4)	0.3212(5)	0.1473(2)	0.080(2)
C(2)	0.1736(4)	0.5817(4)	0.2199(2)	0.066(1)
C(3)	0.2207(3)	0.3222(4)	0.3388(2)	0.061(1)
C(4)	0.0706(4)	0.2736(3)	0.4108(2)	0.054(1)
C(5)	−0.1256(3)	0.2196(3)	0.3780(2)	0.055(1)
C(6)	−0.2170(3)	0.2067(4)	0.2678(2)	0.056(1)
C(7)	0.1587(6)	0.2851(5)	0.5223(2)	0.081(2)
C(8)	−0.2859(5)	0.1676(5)	0.4451(3)	0.087(2)
C(9)	−0.1999(5)	0.1984(6)	0.0886(2)	0.088(2)
C(10)	−0.1193(5)	−0.0293(4)	0.1894(2)	0.071(2)
F(1)	0.2308(4)	0.3284(5)	0.0477(2)	0.149(2)
F(2)	0.4843(3)	0.4617(3)	0.1748(2)	0.109(1)
F(3)	0.2990(3)	0.1462(3)	0.1501(2)	0.138(2)
F(4)	0.0588(3)	0.6324(3)	0.2704(2)	0.111(1)
F(5)	0.1474(7)	0.6357(4)	0.1283(2)	0.185(3)
F(6)	0.3641(4)	0.7209(3)	0.2629(3)	0.133(2)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}\bar{a}_i \cdot \bar{a}_j a_i^* a_j^*$.

Table 4

Positional and equivalent isotropic temperature factors [a] for IV

Atom	*x*	*y*	*z*	*U*
B	−0.1042(7)	0.4192(4)	0.7270(4)	0.054(2)
N	−0.2331(5)	0.4592(3)	0.7967(3)	0.053(1)
C(1)	−0.1658(8)	0.3104(4)	0.6787(5)	0.072(2)
C(2)	0.0982(8)	0.4071(5)	0.7842(5)	0.078(3)
C(3)	−0.1054(7)	0.4995(4)	0.6417(4)	0.065(2)
C(4)	−0.2676(7)	0.5588(4)	0.6098(3)	0.061(2)
C(5)	−0.4058(7)	0.5489(4)	0.6524(4)	0.063(2)
C(6)	−0.4080(6)	0.4812(4)	0.7347(4)	0.061(2)
C(7)	−0.261(1)	0.6290(5)	0.5294(5)	0.091(3)
C(8)	−0.5773(9)	0.6030(6)	0.6209(5)	0.102(3)
C(9)	−0.2557(8)	0.3802(5)	0.8701(4)	0.083(3)
C(10)	−0.364(1)	0.4042(5)	0.9450(5)	0.103(3)
C(11)	−0.1589(8)	0.5534(4)	0.8469(4)	0.071(2)
C(12)	−0.2784(9)	0.6284(4)	0.8786(5)	0.093(3)
F(1)	−0.0807(5)	0.2859(3)	0.6088(3)	0.105(2)
F(2)	−0.1263(6)	0.2327(3)	0.7408(3)	0.129(2)
F(3)	−0.3329(5)	0.2982(3)	0.6412(3)	0.113(2)
F(4)	0.2004(4)	0.3671(3)	0.7294(3)	0.119(2)
F(5)	0.1301(5)	0.3555(4)	0.8646(4)	0.162(3)
F(6)	0.1840(4)	0.4932(3)	0.8130(3)	0.118(2)

[a] See Table 3.

Table 5

Positional and equivalent isotropic temperature factors [a] for IX

Atom	*x*	*y*	*z*	*U*
B	0.211(1)	0.3368(8)	0.2264(7)	0.075(4)
N	0.1785(7)	0.2862(5)	0.3428(4)	0.068(2)
O	0.1118(6)	0.4290(4)	0.2094(4)	0.084(2)
C(1)	0.174(1)	0.2512(9)	0.1284(7)	0.099(4)
C(2)	0.394(1)	0.376(1)	0.2180(9)	0.104(5)
C(3)	−0.0408(9)	0.4306(7)	0.2399(6)	0.075(3)
C(4)	−0.093(1)	0.3581(8)	0.3034(8)	0.089(4)
C(5)	0.0017(9)	0.2679(7)	0.3464(7)	0.086(4)
C(6)	−0.132(1)	0.5247(7)	0.2003(7)	0.095(4)
C(7)	0.235(1)	0.3672(8)	0.4262(7)	0.104(4)
C(8)	0.160(1)	0.377(1)	0.526(1)	0.165(7)
C(9)	0.265(1)	0.1840(6)	0.3585(7)	0.084(4)
C(10)	0.245(1)	0.1263(8)	0.4622(7)	0.113(4)
F(1)	0.2861(7)	0.1797(5)	0.1171(4)	0.131(3)
F(2)	0.0371(8)	0.1949(5)	0.1323(4)	0.129(3)
F(3)	0.1510(9)	0.2997(5)	0.0341(5)	0.159(4)
F(4)	0.5080(6)	0.3076(5)	0.2474(6)	0.154(3)
F(5)	0.4332(7)	0.4627(5)	0.2713(7)	0.156(4)
F(6)	0.4187(8)	0.3982(6)	0.1153(6)	0.173(4)

[a] See Table 3.

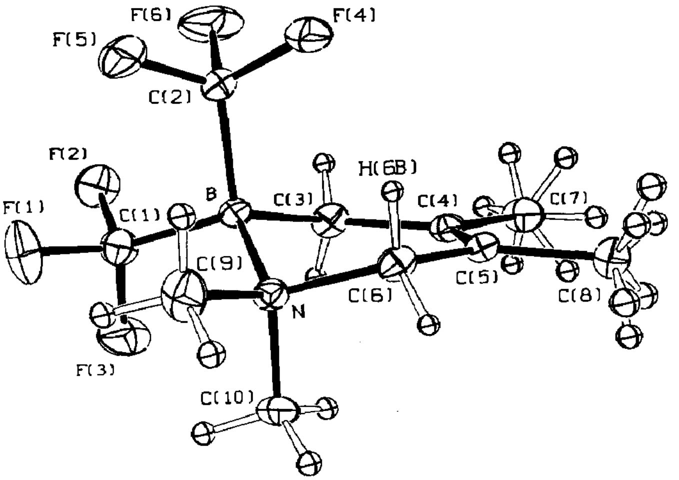


Fig. 1. A perspective drawing of III showing the disordered hydrogen atoms bonded to C(7) and C(8). Nonhydrogen atoms have 13% probability thermal ellipsoids, those of the hydrogen atoms being artificially reduced.

The boron and nitrogen atoms are displaced to opposite sides of these planes, the displacement of the boron atoms (0.087–0.265 Å) always being less than that of the nitrogen atoms (0.458–0.631 Å). Cremer–Pople analyses [16] of the ring puckering indicate that the conformations all lie between canonical half-chair and half-boat forms.

Some bond distances and angles in III, IV and IX are compared with those of $(CF_3)_2BF \cdot NHMe_2$ (**F**) and $(CF_3)_2BOH \cdot NHMe_2$ (**G**) [17] in Table 7. While differences in the B–N distances in the cyclic compounds are barely detectable, these linkages are significantly longer than those in **F** and **G**. Similarly the average $B-CF_3$ bond lengths in III, IV and IX are longer than those in **F** and **G**, and the differences are statistically significant for III, the structure determined most precisely in the present study. Furthermore, the CF_3-B-CF_3 bond angles are distinctly smaller in

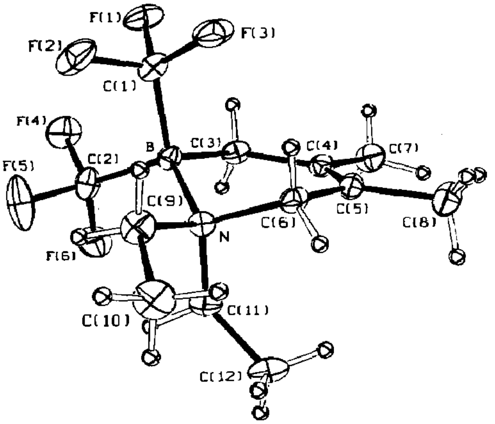


Fig. 2. A perspective drawing of IV with 13% probability thermal ellipsoids for the nonhydrogen atoms and arbitrary spheres for the hydrogen atoms.

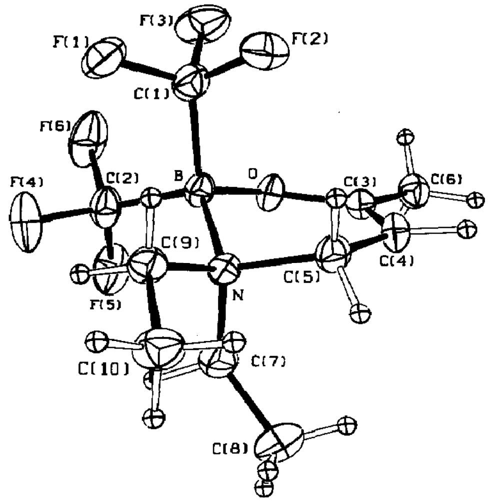


Fig. 3. A perspective drawing of IX with 13% probability thermal ellipsoids for the nonhydrogen atoms and arbitrary spheres for the hydrogen atoms.

the cyclic compounds. The smaller C–B–C angles shorten the F $\cdots$ F distances between CF_3 groups by 0.15–0.20 Å, roughly staggered conformations for the CF_3 groups being found in all of these molecules.

Table 6

Selected bond distances (Å) and angles (°) in III, IV and IX

III		IV		IX	
B–C(1)	1.638(3)	B–C(1)	1.650(8)	B–C(1)	1.66(1)
B–C(2)	1.639(3)	B–C(2)	1.631(8)	B–C(2)	1.63(1)
B–N	1.621(3)	B–N	1.633(6)	B–N	1.64(1)
B–C(3)	1.599(3)	B–C(3)	1.623(8)	B–O	1.45(1)
C(3)–C(4)	1.502(3)	C(3)–C(4)	1.487(7)	O–C(3)	1.363(9)
C(4)–C(5)	1.317(3)	C(4)–C(5)	1.342(7)	C(3)–C(4)	1.32(1)
C(5)–C(6)	1.501(3)	C(5)–C(6)	1.485(7)	C(4)–C(5)	1.48(1)
N–C(6)	1.509(3)	N–C(6)	1.496(6)	N–C(5)	1.506(9)
N–C(9)	1.495(3)	N–C(9)	1.524(7)	N–C(7)	1.52(1)
N–C(10)	1.507(3)	N–C(11)	1.513(6)	N–C(9)	1.499(9)
C(1)–B–C(2)	106.3(2)	C(1)–B–C(2)	106.9(5)	C(1)–B–C(2)	106.5(8)
C(1)–B–N	111.5(2)	C(1)–B–N	112.5(4)	C(1)–B–N	111.6(7)
C(2)–B–N	111.3(2)	C(2)–B–N	112.4(4)	C(2)–B–N	113.5(7)
C(1)–B–C(3)	110.4(2)	C(1)–B–C(3)	109.0(4)	C(1)–B–O	110.5(7)
C(2)–B–C(3)	110.0(2)	C(2)–B–C(3)	107.4(4)	C(2)–B–O	105.9(7)
C(3)–B–N	107.4(2)	C(3)–B–N	108.5(4)	O–B–N	108.6(6)
B–C(3)–C(4)	116.9(2)	B–C(3)–C(4)	117.7(5)	B–O–C(3)	120.9(7)
C(3)–C(4)–C(5)	121.8(2)	C(3)–C(4)–C(5)	121.2(5)	O–C(3)–C(4)	121.4(8)
C(4)–C(5)–C(6)	123.7(2)	C(4)–C(5)–C(6)	123.5(5)	C(3)–C(4)–C(5)	125.1(8)
C(5)–C(6)–N	115.4(2)	C(5)–C(6)–N	115.6(4)	C(4)–C(5)–N	111.9(7)
C(6)–N–B	109.5(1)	C(6)–N–B	108.5(4)	C(5)–N–B	108.5(6)
		N–C(9)–C(10)	119.0(5)	N–C(7)–C(8)	121.5(9)
		N–C(11)–C(12)	120.3(5)	N–C(9)–C(10)	117.0(7)

Table 7

Comparison of several amine-bis(trifluoromethyl)borane structures

Compound	B–C [a] (Å)	B–N (Å)	C [a]–B–C [a] (°)	Ref.
$(CF_3)_2BF\cdot NHMe_2$	1.612(8)	1.584(7)	112.0(5)	17
$(CF_3)_2BOH\cdot NHMe_2$	1.624(4)	1.602(3)	109.6(2)	17
III	1.638(3)	1.621(3)	106.3(2)	
IV	1.641(13)	1.633(6)	106.9(5)	
IX	1.643(25)	1.641(10)	106.5(8)	

[a] Carbon atom of CF_3 group.

Comparison with the acyclic adducts might imply enhanced steric strain in III, IV and IX. Furthermore, the B–C(3)–C(4) and N–C(6)–C(5) bond angles in III and IV are markedly larger than the tetrahedral value. In this connection we note that in each molecule four or five F ··· H contacts are < 2.5 Å (cf. 2.67 Å for the sum of the van der Waals radii [18]). About half of these involve the exocyclic nitrogen substituents. Fluorine atoms are also close to H(3A) and H(3B) in both III and IV, calculated distances falling between 2.42 and 2.58 Å. While ring puckering with concomitant staggering of the exocyclic substituents relieves some of these steric interactions, other repulsive contacts, such as F(4) ··· H(6B) in III (2.28 Å, Fig. 1), are in fact a consequence of puckering.

Some of the above-mentioned repulsive contacts can be relieved in part by allowing the hydrogen atoms to deviate from the idealized positions. We note that the short contacts are not due to the length chosen for the C–H distances (0.95 Å), trial calculations showing that most contacts are slightly shortened when the C–H distances are increased to 1.095 Å. Nonbonded repulsions can often be relieved by deforming bond angles and twisting away from staggered conformations, and such distortions are evident for the ethyl groups in IV and IX. First their N–C–C angles average 10(2)° larger than the tetrahedral value. Second, the "axial" ethyl groups are rotated about the N–C bonds by about 30° from the staggered conformation. These distortions allow the C(12) ··· H(6A) and C(8) ··· H(5A) contacts in IV and IX, respectively, to be lengthened to 2.50 Å, whereas an idealized geometry (C–C 1.525 Å, N–C–C 109.5°, staggered) as in III would require 2.30 Å contacts.

Discussion of the structures

The steric congestion detected in III, IV and IX should have stereochemical consequences. First, the observed order of reactivity of $(CF_3)_2BNR_2$ towards dienes (R = Me > R = Et) probably has a steric origin. Second, the presence of a hydrocarbyl group in three of the four exocyclic sites of the C(3) and C(6) atoms in III and IV is incompatible with the observed structures, only the equatorial position of C(6) is not being crowded by the CF_3 groups. Third, the failure of cyclopentadiene or 1,3-cyclohexadiene to undergo [2 + 4] cycloaddition with $(CF_3)_2BNR_2$ may well be due to CF_3 ··· R repulsions, since the resultant bicycloheptene or bicyclooctene ring requires eclipsed conformations for the B–N bond.

Compounds III and IV are the first structurally characterized species in which a boron atom is bonded to both trifluoromethyl and hydrocarbyl groups. Of these B–C bonds, the average B–CF_3 distances are longer in both cases, but only in III is the difference statistically significant (0.039(4) Å). In this case the distance to the hydrocarbyl group (B–C(3), 1.599(3) Å) appears to be remarkably short for an overcrowded molecule (cf. 1.618(9) Å in Me_3BNMe_2 [19]). Perhaps this reflects the inductive effect of the CF_3 groups, but studies on acyclic compounds would be necessary to clear up this point.

Experimental

IR spectra were recorded with KBr pellets, Raman spectra were of crystalline solids, excitation Kr^+ 647.1 nm.

1,1,4,5-Tetramethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclohex-4-ene (III). Dry 2,3-dimethyl-1,3-butadiene (~ 20 ml) was added to a stirred, icecooled solution of 15 mmol I in 10 ml of dry pentane. Stirring was continued for 1 h at ~ 0 °C and then for 2 h at room temperature. After removal of the solvent and the excess of diene, the residue was sublimed in vacuo (bath temperature 20–40 °C). Yield, 85%. Elemental analyses are set out in Table 8. MS: $m/e = 275$, M^+, 18%; 156, $[M - CF_3 - CF_2]^+$, 26%, 113, $[C_7H_{15}N]^+$, 18%; 82, $[\text{diene}]^+$, 100%; 67, $[\text{diene} - CH_3]^+$, 58% (^{11}B fragments). IR/Raman (cm^{-1}): 1692 vw/s, ν(C=C); 1099 vs/m, 1084 vs/m, $\nu(CF_3)$; 707 -/vs, 700 m/-, $\delta_s(CF_3)$.

Compounds I–XIII and XV. These were obtained analogously, and had properties as follows.

Table 8

Elemental analyses

Compound	Formula	Analyses (Found (calc.) (%))		
		C	H	F
III	$C_{10}H_{16}BF_6N$	43.8	5.8	41.3
		(43.67)	(5.86)	(41.44)
IV	$C_{12}H_{20}BF_6N$	47.9	6.8	38.0
		(47.55)	(6.65)	(37.61)
V	$C_9H_{14}BF_6N$	41.59	5.5	43.3
		(41.41)	(5.41)	(43.67)
VI	$C_{11}H_{18}BF_6N$	45.9	6.4	39.2
		(45.71)	(6.28)	(39.43)
VII	$C_{10}H_{16}BF_6N$	43.7	6.0	41.5
		(43.67)	(5.86)	(41.44)
VIII	$C_8H_{12}BF_6NO$	36.4	4.6	43.6
		(36.54)	(4.60)	(43.34)
IX	$C_{10}H_{16}BF_6NO$	41.7	5.7	38.5
		(41.27)	(5.54)	(39.17)
X	$C_9H_{14}BF_6NO_2$	36.8	4.9	38.6
		(36.89)	(4.82)	(38.90)
XI	$C_9H_{14}BF_6NO$	38.9	5.0	41.3
		(39.02)	(5.09)	(41.15)
XII	$C_9H_{14}BF_6NO_2$	36.9	5.14	39.2
		(36.89)	(4.82)	(38.90)
XIII	$C_{12}H_{18}BF_6NO$	45.2	5.6	35.7
		(45.45)	(5.72)	(35.95)
XV	$C_8H_{16}BF_6NO$	40.4	5.4	40.0
		(41.27)	(5.54)	(39.17)

1,1-Diethyl-2,2-bis(trifluoromethyl)-4,5-dimethyl-1-azonia-2-borata-cyclohex-4-ene (IV). MS: $m/e = 303$, M^+, 8%; 184, $[M - CF_3 - CF_2]^+$, 16%; 86, $[C_5H_{12}N]^+$, 23%; 82, $[\text{diene}]^+$, 100%. IR/Raman (cm^{-1}): 1694 w/m, $\nu(C{=}C)$; 1126, s/-, 1112 s/-, 1090 vs/w, $\nu(CF_3)$; 707 m/s, 668 m/m, $\delta_s(CF_3)$.

1,1,4-Trimethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclohex-4-ene (V). MS: $m/e = 261$, M^+, 8%; 142, $[M - CF_3 - CF_2]^+$, 23%; 99, $[C_6H_{13}N]^+$, 23%; 68, $[\text{diene}]^+$, 100%. IR/Raman (cm^{-1}): 1689 w/m, $\nu(C{=}C)$; 1123 s/-, 1088 vs/w, $\nu(CF_3)$; 705 -/vs, 700 m/-, $\delta_s(CF_3)$.

1,1-Diethyl-2,2-bis(trifluoromethyl)-4-methyl-1-azonia-4-borata-cyclohex-4-ene (VI). MS: $m/e = 289$, M^+, 4%; 170, $[M - CF_3 - CF_2]^+$, 12%; 106 $[F_2BNC_3H_7]^+$, 16%; 68, $[\text{diene}]^+$, 100%. IR/Raman (cm^{-1}): 1692 vw/m, $\nu(C{=}C)$; 1096 s/m, 1088 vs/-, $\nu(CF_3)$; 705 m/vs, 672 m/w, $\delta_s(CF_3)$.

1,1,4,6-Tetramethyl-2,2-bis(trifluoromethyl)-1-azonia-2-borata-cyclohex-4-ene (VII). MS: $m/e = 275$, M^+, 7%; 156, $[M - CF_3 - CF_2]^+$, 19%; 82, $[\text{diene}]^+$, 100%; 67, $[\text{diene} - CH_3]^+$, 43%. IR/Raman (cm^{-1}): 1683 w/m, $\nu(C{=}C)$; 1092 vs/m, 1086 vs/-, $\nu(CF_3)$; 700 -/s, 681 s/-, $\delta_s(CF_3)$.

3,3,6-Trimethyl-2,2-bis(trifluoromethyl)-3-azonia-2-borata-oxacyclohex-5-ene (VIII). MS: $m/e = 263$, M^+, 22%; 144, $[M - CF_3 - CF_2]^+$, 100%; 90 $[FB(O)N(CH_3)_2]^+$, 80%. IR/Raman (cm^{-1}): 1692 m/m, $\nu(C{=}C)$; ~ 1100 vsb/w, $\nu(CF_3)$; 711 m/s, 688 m/-, $\delta_s(CF_3)$.

3,3-Diethyl-2,2-bis(trifluoromethyl)-6-methyl-3-azonia-2-borata-oxacyclohex-5-ene (IX). MS: $m/e = 291$, M^+, 20%; 176, $[M - 2CF_2 - CH_3]^+$, 65%; 172, $[M - CF_3 - CF_2]^+$, 100%; 118, $[FB(O)N(C_2H_5)_2]^+$, 75%; 106, $[F_2BNC_3H_7]^+$, 90%. IR/Raman (cm^{-1}): 1690 m/m, $\nu(C{=}C)$; 1102 s/w, 1088 vs/vw, $\nu(CF_3)$; 713 m/vs, 694 m/w, $\delta_s(CF_3)$.

3,3,5-Trimethyl-2,2-bis(trifluoromethyl)-6-methoxy-3-azonia-2-borata-oxacyclohex-5-ene (X). MS: $m/e = 293$, M^+, 8%; 224, $[M - CF_3]^+$, 12%; 174, $[M - CF_3 - CF_2]^+$, 11%; 92, $[F_2BNC_2H_5]^+$, 16%; 69, $[CF_3]^+$, 100%. IR/Raman (cm^{-1}): 1721 s/s, $\nu(C{=}C)$; 1120 vs/-, 1084 vs/w, $\nu(CF_3)$; 715 m/vs, 698 m/-, $\delta_s(CF_3)$.

3,3,4,5-Tetramethyl-2,2-bis(trifluoromethyl)-3-azonia-2-borata-oxacyclohex-5-ene (XI). MS: $m/e = 277$, M^+, 24%; 208, $[M - CF_3]^+$, 14%; 162 $[M - 2CF_2 - CH_3]^+$, 50%; 158, $[M - CF_3 - CF_2]^+$, 94%; 90, $[FB(O)N(CH_3)_2]^+$, 100%. IR/Raman (cm^{-1}): 1675 s/m, $\nu(C{=}C)$; 1103 vs/w, 1088 vs/-, $\nu(CF_3)$; 719 w/vs, 701 s/w, $\delta_s(CF_3)$.

3,3,5-Trimethyl-2,2-bis(trifluoromethyl)-4-methoxy-3-azonia-2-borata-oxacyclohex-5-ene (XII). MS: $m/e = 293$, M^+, 0.3%; 224, $[M - CF_3]^+$, 11%; 174, $[M - CF_3 - CF_2]^+$, 3%; 100, $[\text{enone}]^+$, 26%; 85, $[\text{enone} - CH_3]^+$, 100%. IR/Raman (cm^{-1}): 1688 s/s, $\nu(C{=}C)$; 1100 vs/w, 1088 vs/w, $\nu(CF_3)$; 709 m/vs, 700 s/-, $\delta_s(CF_3)$.

2,5,5-Trimethyl-4,4-bis(trifluoromethyl)-3-oxa-5-azonia-4-borata-bicyclo[4.4.0]dec-1-ene (XIII). MS: $m/e = 317$, M^+, 15%; 248, $[M - CF_3]^+$, 34%; 198, $[M - CF_3 - CF_2]^+$, 100%; 124, $[\text{enone}]^+$, 32%; 92, $[C_7H_8]^+$, 50%. IR/Raman (cm^{-1}): 1690 m/vs, $\nu(C{=}C)$; 1102 vs/w, 1090 vs/-, $\nu(CF_3)$; 715 w/vs, 698 m/-, $\delta_s(CF_3)$.

Bis(trifluoromethyl)-(4-methyl-3-penten-2-on-1-yl)borane-dimethylamine (XV) was recovered upon attempting to isolate XIV by sublimation. MS: $m/e = 291$, M^+, 11%; 272, $[M - F]^+$, 2%; 94, $[C_6H_6O]^+$, 23%; 83, $[C_5H_7O]^+$, 100%. IR/Raman (cm^{-1}): 3153 s/-, $\nu(NH)$; 1662 vs/m, $\nu(C{=}O)$; 1610 m/s, $\nu(C{=}C)$; 1085 s/vw, $\nu(CF_3)$; 711 w/vs, $\delta_s(CF_3)$.

Acknowledgements

We wish to thank the Fonds der Chemie for financial support.

References

1 P. Paetzold, Adv. Inorg. Chem. Radiochem., 31 (1987) 286.
2 L.R. Thorne, R.D. Suenram and F.J. Lovas, J. Chem. Phys., 78 (1983) 167.
3 M. Sugie, H. Takeo and C. Matsumura, J. Mol. Spectrosc., 123 (1987) 286.
4 A. Haaland, Angew. Chem., 101 (1989) 1017.
5 D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke and W. Weuter, J. Organomet. Chem., 378 (1989) 125.
6 D.J. Brauer, H. Bürger, F. Dörrenbach, B. Krumm, G. Pawelke and W. Weuter, J. Organomet. Chem., 385 (1990) 161.
7 R. Hausser-Wallis, H. Oberhammer, H. Bürger and G. Pawelke, J. Chem. Soc., Dalton Trans., (1987) 1839.
8 K. Niedenzu and J.W. Dawson, Boron-Nitrogen Compounds, Springer, Berlin (1965).
9 P. Paetzold and G. Schimmel, Z. Naturforsch., 35b (1980) 568.
10 H. Bürger, M. Grunwald and G. Pawelke, J. Fluorine Chem., 31 (1986) 89.
11 A.G. Brook, K. Vorspohl, R.R. Ford, M. Hesse and W.J. Chatterton, Organometallics, 6 (1987) 2128.
12 N. Wiberg and K. Schurz, J. Organomet. Chem., 341 (1988) 145.
13 International Tables for X-Ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, 1974, Tables 2.2 B and 2.3.1.
14 G.M. Sheldrick, SHELX-76: Program for crystal structure determination, University of Cambridge, Cambridge, 1976.
15 Additional crystallographic tables may be obtained from Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD 54750, the names of the authors and the literature reference.
16 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.
17 D.J. Brauer, H. Bürger, G. Pawelke, W. Weuter and J. Wilke, J. Organomet. Chem., 329 (1987) 293.
18 A. Bondi, J. Phys. Chem., 68 (1964) 441.
19 K. Ouzounis, H. Riffel and H. Hess, J. Organomet. Chem., 332 (1987) 253.