

[2 + 3] Cycloaddition reactions of dimethylamino-bis(trifluoromethyl) borane, $(CF_3)_2BNMe_2$, with nitrile oxides, nitrones and $Me_2C=SO_2$. Crystal and molecular structure of $(CF_3)_2B-NMe_2-{}^1BuC=N-O$ and $(CF_3)_2B-NMe_2-CMe_2-S(=O)-O$ ¹

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Abstract

Dimethylamino-bis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (A), undergoes [2 + 3] cycloaddition reactions with various 1,3 dipolar species to yield five-membered heterocycles. While nitrile oxides $RCNO$ give $(CF_3)_2B-NMe_2-RC=N-O$; R = Mes (I), Ph (II), pClC_6H_4 (III), tBu (IV), iPr (V), nitrones $R^1HC=N(R^2)-O$ furnish the thermally less stable and moisture sensitive heterocycles $(CF_3)_2B-NMe_2-R^1HC-NR^2-O$; R² = Me, R¹ = Ph (VI), pClC_6H_4 (VII), C_6F_5 (VIII), tBu (IX), iPr (X); R² = R¹ = Ph (XI). Analogously, $Me_2C=SO_2$ yields the five-membered ring $(CF_3)_2B-NMe_2-CMe_2-S(=O)-O$ (XII). The constitution of the novel boron compounds has been deduced from multinuclear NMR, IR and mass spectra. The structures of IV and XII have been investigated by single-crystal X-ray diffraction.

Keywords: Boron; Dimethylamino-bis(trifluoromethyl)borane; Cycloaddition reactions

1. Introduction

Dimethylamino-bis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (A), 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. In preceding contributions from our laboratory we have reported on numerous [2 + 4] and [2 + 2] cycloaddition reactions of A. Thus A combines with 1,3 unsaturated compounds of the general formula $X=CR^3-CR^2=CHR^1$ (X = CH₂, O) to form novel six-membered heterocycles $(CF_3)_2B-NMe_2-CHR^1-CR^2=CR^3-X$ in high yields [2]. Isocyanates and isothiocyanates $R-N=C=X$ (X = O, S) react with A to yield two types of four-membered ring, $(CF_3)_2B-NMe_2-C(=X)-NR$ and $(CF_3)_2B-X-C(=NMe_2)-NR$, depending on the nature of R [3].

However, no examples of [2 + 3] cycloaddition reactions of A had been discovered previously. Such reactions of aminoboranes and the 1,3 dipolar imine oxide (nitron) $PhHC=N(Me)-O$ have already been studied [4], but only Cl_2BNMe_2 gave a stable heterocyclopentane derivative, $Cl_2B-NMe_2-PhHC-NMe-O$. The corresponding cycloadduct obtained at low temperature from Me_2BNMe_2 and $PhHC=N(Me)-O$ was found by NMR spectroscopy to be in equilibrium with the reactants according to



Since the Lewis acidity of boron in A in comparison with that in Me_2BNMe_2 might carry reaction (1) to stable [2 + 3] cycloadducts, we have investigated reactions of A with imine oxides.

To our knowledge no [2 + 3] cycloaddition reactions of dialkyl or dihalo aminoboranes with nitrile oxides

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¹ Dedicated to Professor Kurt Dehnicke on the occasion of his 65th birthday.

R-CNO have yet been reported. Nitrile oxides are commonly accepted as reactive 1,3 dipolar reactants [5], and the high reactivity of the B=N double bond in A prompted us to investigate its reactions with such nitrile oxides and to study the effect of fluorine substitution on the synthesis and stability of [2 + 3] cycloadducts with nitrones.

While investigating [2 + 2] cycloaddition reactions of A with various heterocumulenes (N-sulfinyl-sulfonamides, amino-iminophosphanes, etc.), we discovered that some sulfenes reveal a behavior in agreement with a 1,3 dipolar character. The results of the reaction with sulfenes will also be reported.

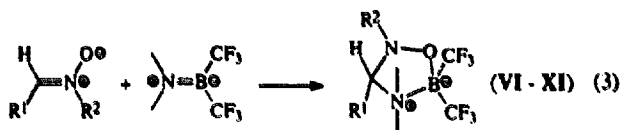
2. Results

The aminoborane A reacts with the nitrile oxides RCNO according to Eq. (2) to give the corresponding novel five-membered heterocycles $(CF_3)_2B-NMe_2-RC=N-O$ (I–V) in yields ranging from 29 (III) to 78% (I). Except for R = Mes, all the above-mentioned nitrile oxides readily dimerize; therefore they were prepared at $-30^\circ C$ in situ by abstraction of HCl from the corresponding hydroxamic acid chlorides $RCIC=NOH$ using triethylamine. The modest yields of the heterocyclopentenes II–V are probably due to competitive side-reactions involving auto-dimerization of the nitrile oxides.



R = Mes (I), Ph (II), pClC_6H_4 (III), tBu (IV), iPr (V)

In contrast to the nitrile oxides, the imine oxides $R^1HC=N(R^2)-O$, $R^2 = Me$, $R^1 = Ph$, pClC_6H_4 , C_6F_5 , tBu , iPr ; $R^2 = R^1 = Ph$ are stable at room temperature. They react readily with A at $-10^\circ C$ in pentane solution to yield the heterocyclopentanes (VI–XI)



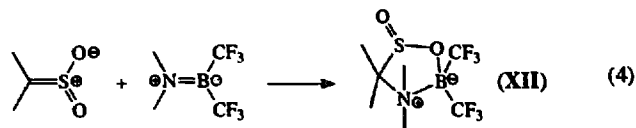
$R^2 = Me$, $R^1 = Ph$ (VI), pClC_6H_4 (VII), C_6F_5 (VIII), tBu (IX), iPr (X);

$R^2 = R^1 = Ph$ (XI)

These were obtained in much better yields (70–80%).

Somewhat unexpectedly, the dimethyl methylene sulfone $Me_2C=SO_2$ also behaved as a 1,3 dipolar reactant

and readily gave a [2 + 3] cycloaddition product (XII) according to Eq. (4). This was isolated in a 63% yield.



However, the related methylene sulfones $PhHC=SO_2$, $MeHC=SO_2$ and $H_2C=SO_2$ did not react cleanly with A, but rather produced black tarry material which could not be characterized.

3. Properties and spectra

The novel boron heterocycles I–XII are colorless solids, the melting points of which are reported in the Experimental section. Compounds I–V and XII are stable to air and moisture and soluble in polar organic solvents, while species VI–XI are sensitive to hydrolysis and therefore have to be handled in a dry atmosphere. They are also thermally less stable than I–V, decomposition occurring between 70 and $105^\circ C$. In particular IX and X, which contain bulky electron donating tBu and iPr groups, apparently have a labile C–NMe₂ bond. Indeed, the mass spectrum of IX mainly contains fragment ions of decomposition products.

The 1H , ^{19}F , ^{11}B and ^{13}C NMR spectra of I–XII were recorded. The chemical shifts, 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 are not detectable due to quadrupole broadening by the boron atom. Compounds VI–XII have an asymmetric ring atom which should cause a splitting of the NMR signals both of the $N(CH_3)_2$ and $B(CF_3)_2$ groups. While only VI–VIII and XII show this expected splitting, the resonances of IX and X are just broadened. The C_6F_5 group of compound VIII reveals five ^{19}F and ^{13}C resonances in spectra recorded at $25^\circ C$. This indicates hindered rotation of the pentafluorophenyl group. However, attempts to determine the barrier to rotation by high temperature ^{19}F NMR spectroscopy failed due to the thermal instability of VIII.

The constitution of compound XII as a five-membered ring follows from the NMR spectra. The fact that $Me_2C=SO_2$ reacts as a 1,3 dipolar species was unexpected because it is well known that sulfenes undergo [2 + 2] cycloaddition reactions, e.g. with enamines [6]. However, the two possible four-membered heterocycles $(CF_3)_2B-NMe_2-CMe_2-SO_2$ and $(CF_3)_2B-NMe_2-SO_2-CMe_2$, as well as the five-membered isomer

$(CF_3)_2B-NMe_2-O-S(=O)-CMe_2$, can be excluded by the following arguments. The ^{13}C signal at 89.4 ppm assigned to $C(CH_3)_2$ is sharp; therefore this carbon atom cannot be bonded to boron, thus ruling out the latter two structures. The splitting of the NCH_3 and

CCH_3 signals, both in the 1H and the ^{13}C spectra, and the two fluorine resonances at -65.5 and -66.4 ppm exclude a symmetrically substituted planar four-membered ring. Moreover, one of the CCH_3 ^{13}C signals at 20 ppm appears as a quartet with a $^5J(CF)$ coupling

Table 1
NMR spectral data for I–XII (δ in ppm)^a

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
1H												
δ (BN(CH ₃) ₂)	2.94	3.06	3.07	3.17	3.00	2.68	2.69	2.87	3.00	2.80	2.75	2.89
δ (CNCH ₃)						2.77	2.77	2.91			2.82	3.25
δ (SC(CH ₃) ₂)						2.68	2.69	2.71	2.89	2.76		1.65
												1.68
δ (CH(CH ₃) ₂)					1.36					1.12		
δ (C(CH ₃) ₃)				1.43					1.22			
δ (CH(CH ₃) ₂)					2.70					2.11		
	2.33											
δ (C ₆ H _n CH ₃)	2.34											
δ (NCHN)						4.58	4.59	4.99	3.56	3.42	5.33	
δ (C ₆ H _n)	7.05	7.48	7.47			7.49	7.55				7.00	
		7.67	7.55			7.54					7.17	
											7.46	
											7.53	
^{19}F												
δ (CF ₃)	-66.3	-66.2	-66.3	-66.5	-66.6	-66.7	-66.2	-64.8	-66.1	-67.1	-66.0	-65.1
						-67.9	-67.4	-66.3				-66.4
								-127.3				
								-135.3				
δ (C ₆ F ₅)								-144.3				
								-156.4				
								-157.1				
^{11}B												
δ (B)	1.9	1.8	1.7	1.9	1.4	1.7	1.3	1.3	1.8	1.9	1.3	3.5
^{13}C												
δ (BN(CH ₃) ₂)	45.6	45.5	45.6	47.0	44.6	42.8	42.8	43.8	44.2	42.7	44.3	44.9
						43.7	43.7	44.7			44.8	50.6
δ (NCHN)						93.5	93.4	86.9	96.3	93.6	91.5	
δ (CNCH ₃)						43.3	43.3	43.2	46.2	44.8		
δ (C(CH ₃) ₃)				29.6					28.8			
δ (C(CH ₃) ₃)				36.7					34.3			
δ (SC(CH ₃) ₂)												17.0
												20.0
δ (CH(CH ₃) ₂)					22.2					23.2		
δ (SC(CH ₃) ₂)												
δ (CH(CH ₃) ₂)					24.0					23.3		
δ (C ₆ H _n CH ₃)	20.8											
	20.9											
δ (C=N)	152.3	156.1	155.3	163.5	161.1						120.9	
δ (C ₆ H _n)	116.9	121.5	120.1			126.2	126.2	101.6			125.5	
(C ₆ F ₅)	129.9	129.4	129.9			128.5	128.4	138.3			126.7	
	140.6	129.9	131.2			129.3	129.2	139.3			128.6	
	142.0	132.3	139.			131.7	130.4	144.1			129.1	
								147.1			131.0	
											131.7	
											147.4	

^a I–III, V–VII and IX–XII in CDCl₃, IV in CD₃CN, VIII in CD₂Cl₂. ¹H: 250.13 MHz, internal standard CHCl₃ 7.27 ppm, CHDCl₂ 5.35 ppm, CD₂HCN 1.95 ppm. ¹³C: 62.9 MHz, internal standard CDCl₃ 77.0 ppm, CD₂Cl₂ 53.8 ppm, CD₃CN 1.30 ppm. ¹⁹F: 84.67 MHz, internal standard CFCI₃. ¹¹B: 25.52 MHz, external standard BF₃·OEt₂.

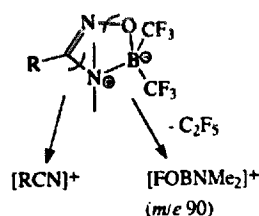


Fig. 1. Fragmentation of compounds I–V.

constant of 5 Hz. This large long range coupling is further proof of the proposed constitution of XII, $(CF_3)_2B-NMe_2-CMe_2-S(=O)-O$. This constitution is also supported by the mass spectral data (vide infra).

EI mass spectral data for I–XII are listed in Table 2. The peaks of the molecular ions M^+ are generally weak if at all detectable, but the ions $[M-CF_3]^+$ and $[M-C_2F_5]^+$ are indicative of the molecular mass. The fragmentation patterns of the heterocyclopentenes I–V on the one hand and the pentanes VI–XI on the other hand are significantly different. While the cycloadducts I–V fracture at the C–NMe₂ and N–O bonds (Fig. 1) to form the characteristic fragments assigned as $[FOBN(CH_3)_2]^+$ and $[RCN]^+$, the fragmentation of VI–XI is more complicated. Here the characteristic ions are $[R^1-CH=NOMe]^+$, $[R^1-CNOMe]^+$, $[R^1CNMe]^+$ and the ion m/e 92, which is assigned to $[F_2BN(=CH_2)CH_3]^+$.

The base peak of compound XII is m/e 86, which is assigned to the fragment $[(CH_3)_2NC(CH_3)_2]^+$. A further characteristic ion in the mass spectrum of XII is m/e 90, which can be ascribed to $[FOBN(CH_3)_2]^+$. The appearance of these two fragments, and the absence

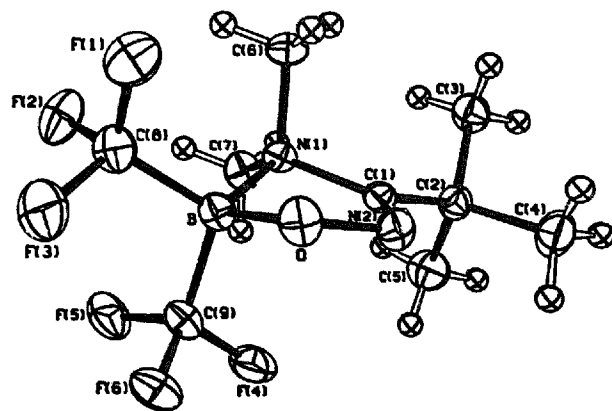


Fig. 2. A perspective drawing of IV with 20% probability thermal ellipsoids except for the hydrogen atoms.

of infrared bands which can be assigned to an SO₂ group, strongly support the proposed constitution $(CF_3)_2B-NMe_2-CMe_2-S(=O)-O$ of XII.

The infrared spectra of compounds I–V show the characteristic (C=N) stretching vibrations between 1600 and 1660 cm⁻¹, while XII has a strong absorption at 1002 cm⁻¹ which might be attributed to an (S=O) stretching mode.

4. Description of the crystal structures of IV and XII

The X-ray studies confirm the proposed structures. Thus IV contains a five-membered ring (Fig. 2) which exhibits C(1)–N(2) (1.264(3) Å) and N(2)–O (1.411(2)

Table 2

Selected electron impact mass spectral data in order of decreasing intensity (m/e (relative intensity (%)) [fragment]⁺) for I–XII

I	44(100)[N(CH ₃) ₃] ⁺ /130(74)[C ₆ H ₈ N] ⁺ /144(69)[C ₁₀ H ₁₀ N] ⁺ /146(64)[C ₁₀ H ₁₂ N] ⁺ /235(44)[M–C ₂ F ₅] ⁺ /145(40)[C ₁₀ H ₁₁ N] ⁺ /77(34)[C ₆ H ₇] ⁺ /189(31)[C ₁₂ H ₁₇ N ₂] ⁺ /254(26)[M–C ₂ F ₃] ⁺ /103(24)[C ₆ H ₅ CN] ⁺ /285(23)[M–CF ₃] ⁺ /90(21)[FOBN(CH ₃) ₂] ⁺ /304(8)[M–CF ₂] ⁺ /354(5)[M] ⁺
II	90(100)[FOBN(CH ₃) ₂] ⁺ /44(94)[N(CH ₃) ₃] ⁺ /193(75)[M–C ₂ F ₅] ⁺ /104(53)[C ₆ H ₆ CN] ⁺ /103(26)[C ₆ H ₅ CN] ⁺ /243(24)[M–CF ₃] ⁺ /77(39)[C ₆ H ₅] ⁺ /212(4)[M–C ₂ F ₅] ⁺ /312(1)[M] ⁺
III	90(100)[FOBN(CH ₃) ₂] ⁺ /44(94)[N(CH ₃) ₃] ⁺ /227(55)[M–C ₂ F ₅] ⁺ /138(43)[C ₁₀ H ₈ CN] ⁺ /75(33)[C ₆ H ₅] ⁺ /102(31)[C ₆ H ₄ CN] ⁺ /137(27)[C ₁₀ H ₇ CN] ⁺ /277(17)[M–CF ₃] ⁺ /111(15)[C ₁₀ H ₇] ⁺ /246(11)[M–C ₂ F ₅] ⁺ /181(5)[C ₁₀ H ₁₀ N ₂] ⁺ /346(3)[M] ⁺
IV	44(100)[N(CH ₃) ₃] ⁺ /90(65)[FOBN(CH ₃) ₂] ⁺ /57(64)[C(CH ₃) ₃] ⁺ /173(55)[M–C ₂ F ₅] ⁺ /117(54)[M–C ₂ F ₅ –H ₂ C=C(CH ₃) ₂] ⁺ /92(14)[F ₂ BN(=CH ₂)CH ₃] ⁺ /71(16)[HN(CN)(CH ₃) ₂] ⁺ /70(11)[OBNCH ₂ (CH ₃)] ⁺ /223(9)[M–CF ₃] ⁺
V	44(100)[N(CH ₃) ₃] ⁺ /90(58)[FOBN(CH ₃) ₂] ⁺ /159(35)[M–C ₂ F ₅] ⁺ /70(10)[OBNCH ₂ (CH ₃)] ⁺ /74(10)[FBN(CH ₃) ₂] ⁺ /209(7)[M–CF ₃] ⁺
VI	92(100)[F ₂ BN(=CH ₂)CH ₃] ⁺ /118(91)[C ₆ H ₅ CNCH ₃] ⁺ /134(78)[C ₈ H ₆ NO] ⁺ /42(61)[(CH ₂) ₂ N] ⁺ /135(61)[C ₈ H ₁₀ NO] ⁺ /77(42)[C ₆ H ₅] ⁺ /259(29)[M–CF ₃] ⁺ /209(24)[M–C ₂ F ₅] ⁺ /328(6)[M] ⁺
VII	92(100)[F ₂ BN(=CH ₂)CH ₃] ⁺ /42(92)[(CH ₂) ₂ N] ⁺ /168(66)[C ₁₀ H ₈ NO] ⁺ /77(48)[C ₆ H ₅] ⁺ /169(47)[C ₁₀ H ₆ NO] ⁺ /152(26)[C ₁₀ H ₇ CNCH ₃] ⁺ /243(6)[M–C ₂ F ₅] ⁺ /293(6)[M–CF ₃] ⁺ /362(2)[M] ⁺
VIII	42(100)[(CH ₂) ₂ N] ⁺ /92(91)[F ₂ BN(=CH ₂)CH ₃] ⁺ /208(37)[C ₆ F ₅ CNCH ₃] ⁺ /349(10)[M–CF ₃] ⁺ /299(7)[M–C ₂ F ₅] ⁺ /418(3)[M] ⁺
IX	92(100)[F ₂ BN(=CH ₂)CH ₃] ⁺ /42(70)[(CH ₂) ₂ N] ⁺ /70(44)[C ₂ H ₆ N ₂] ⁺ /55(41)[C ₄ H ₇] ⁺ /115(37)[(CH ₃) ₃ CCHNOCH ₃] ⁺ /74(28)[FBN(CH ₃) ₂] ⁺ /100(19)[C ₈ H ₁₀ NO] ⁺ /124(17)[M–C ₂ F ₅ –C(CH ₃) ₃ –HCN] ⁺ /151(12)[M–C ₂ F ₅ –C(CH ₃) ₃] ⁺ /174(7)[M–C ₂ F ₅ –CH ₃] ⁺ /239(5)[M–CF ₃] ⁺ /189(3)[M–C ₂ F ₅] ⁺ /308(3)[M] ⁺
X	42(100)[(CH ₂) ₂ N] ⁺ /92(83)[F ₂ BN(=CH ₂)CH ₃] ⁺ /101(20)[(CH ₃) ₂ CHCHNOCH ₃] ⁺ /124(10)[M–C ₂ F ₅ –CH(CH ₃) ₂ –HCN] ⁺ /175(7)[M–C ₂ F ₅] ⁺ /151(4)[M–C ₂ F ₅ –CH(CH ₃) ₂] ⁺ /225(4)[M–CF ₃] ⁺ /294(2)[M] ⁺
XI	91(100)[NC ₆ H ₅] ⁺ /77(77)[C ₆ H ₅] ⁺ /92(56)[F ₂ BN(=CH ₂)CH ₃] ⁺ /180(23)[C ₆ H ₅ CNC ₆ H ₅] ⁺ /196(11)[C ₆ H ₅ CNOC ₆ H ₅] ⁺ /321(4)[M–CF ₃] ⁺ /390(2)[M] ⁺
XII	86(100)[(CH ₃) ₂ NC(CH ₃) ₂] ⁺ /41(58)[CH ₃ CN] ⁺ /56(47)[CH ₃ NCCH ₃] ⁺ /70(35)[(CH ₃) ₂ CNCH ₂] ⁺ /92(21)[F ₂ BN(=CH ₂)CH ₃] ⁺ /90(12)[FOBN(CH ₃) ₂] ⁺ /180(9)[M–C ₂ F ₅] ⁺ /134(7)[(CH ₃) ₂ NC(CH ₃) ₂ SO] ⁺ /120(7)[FBOSNC ₂ H ₄] ⁺ /230(2)[M–CF ₃] ⁺

Table 3
Selected bond distances (Å) and angles (°) in IV

B–C(8)	1.624(4)	C(2)–C(3)	1.532(3)
B–C(9)	1.628(4)	C(2)–C(4)	1.535(3)
B–N(1)	1.612(3)	C(2)–C(5)	1.531(4)
B–O	1.443(3)	C(8)–F(1)	1.336(3)
N(1)–C(1)	1.503(2)	C(8)–F(2)	1.341(3)
N(1)–C(6)	1.514(3)	C(8)–F(3)	1.350(3)
N(1)–C(7)	1.497(2)	C(9)–F(4)	1.347(3)
N(2)–C(1)	1.264(3)	C(9)–F(5)	1.350(3)
N(2)–O	1.411(2)	C(9)–F(6)	1.355(3)
C(1)–C(2)	1.518(3)		
C(8)–B–C(9)	109.3(2)	C(1)–N(1)–C(6)	106.5(2)
C(8)–B–N(1)	114.8(2)	C(1)–N(1)–C(7)	117.3(2)
C(8)–B–O	110.9(2)	C(6)–N(1)–C(7)	107.7(2)
C(9)–B–N(1)	111.2(2)	O–N(2)–C(1)	111.5(2)
C(9)–B–O	110.3(2)	B–O–N(2)	107.1(2)
N(1)–B–O	100.0(2)	N(1)–C(1)–N(2)	111.8(2)
B–N(1)–C(1)	97.9(1)	N(1)–C(1)–C(2)	126.9(2)
B–N(1)–C(6)	111.4(2)	N(2)–C(1)–C(2)	121.3(2)
B–N(1)–C(7)	115.7(2)		

Å) bond lengths typical of an oxime fragment incapable of π -conjugation to its neighbours – average values in such cases are reported as 1.281(13) and 1.416(6) Å respectively [7]. Furthermore, in agreement with a double bond between the C(1) and N(2) atoms, the O, N(1), N(2), C(1), C(2) fragment is planar to within ± 0.029 Å. The boron atom lies 0.556(3) Å from this plane, the ring being folded along the N(1)···O tie-line by 33.2(4)°. Adoption of the envelope conformation opens the O–B–N(1)–C(1) and N(1)–B–O–N(2) torsion angles to 31.2(4) and $-31.6(4)$ ° respectively. The former torsion combines with deviations in the bond angles of the B and N(1) atoms from the tetrahedral value (Table 3) to reduce steric crowding involving their exocyclic substituents. However, puckering shortens the contacts between the methyl carbon C(7) and the ^tBu group. Here steric repulsion is relieved by opening the C(1)–N(1)–C(7) and N(1)–C(1)–C(2) angles to 117.3(2) and 126.9(2)°, gearing C(7) between the C(3) and C(5)

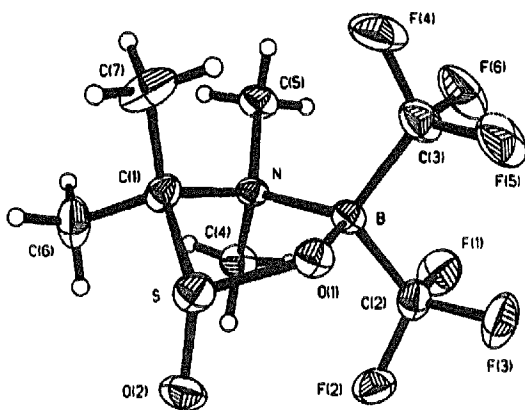


Fig. 3. A perspective drawing of XII with 20% probability thermal ellipsoids except for the hydrogen atoms.

Table 4
Selected bond distances (Å) and angles (°) in XII

B–C(2)	1.646(5)	S–C(1)	1.849(3)
B–C(3)	1.627(4)	C(1)–C(6)	1.514(5)
B–N	1.643(4)	C(1)–C(7)	1.527(5)
B–O(1)	1.470(3)	C(2)–F(1)	1.357(4)
N–C(1)	1.543(3)	C(2)–F(2)	1.337(4)
N–C(4)	1.516(3)	C(2)–F(3)	1.343(4)
N–C(5)	1.509(3)	C(3)–F(4)	1.341(5)
S–O(1)	1.590(2)	C(3)–F(5)	1.347(4)
S–O(2)	1.452(2)	C(3)–F(6)	1.357(5)
C(2)–B–C(3)	106.4(3)	C(4)–N–C(5)	104.0(2)
C(2)–B–N	114.3(2)	B–O(1)–S	118.1(2)
C(2)–B–O(1)	108.4(2)	O(1)–S–O(2)	110.1(1)
C(3)–B–N	115.0(2)	O(1)–S–C(1)	92.4(1)
C(3)–B–O(1)	107.7(2)	O(2)–S–C(1)	107.0(1)
N–B–O(1)	104.8(2)	N–C(1)–S	103.7(2)
B–N–C(1)	106.7(2)	N–C(1)–C(6)	114.2(3)
B–N–C(4)	111.6(2)	N–C(1)–C(7)	112.0(3)
B–N–C(5)	113.8(2)	S–C(1)–C(6)	109.6(2)
C(1)–N–C(4)	109.4(2)	S–C(1)–C(7)	105.3(2)
C(1)–N–C(5)	111.2(2)	C(6)–C(1)–C(7)	111.4(3)

atoms and tilting the C₃ axis of the ^tBu group away from the C(1)–C(2) bond. The B–N(1) (1.612(3) Å) and B–O (1.443(3) Å) bond distances in IV do not differ significantly from the corresponding distances in the six-membered ring (CF₃)₂B–NEt₂–CH₂–CH–CMe–O (1.64(1) and 1.45(1) Å respectively [2]). That these values are significantly shorter than the analogous bond lengths in the five-membered ring Ph₂B–NMe₂–CH₂–CH₂–O (1.686(2) and 1.470(2) Å respectively [8]) can be attributed in part to the inductive effect of the CF₃ groups.

The heterocycle of XII (Fig. 3) possesses a twist conformation with the boron atom on the pseudo-two-fold axis. Although the endocyclic bond angles of the B, N and O(1) atoms in XII are 4.8(4), 8.8(2) and 11.0(3)° larger than the corresponding angles in IV, the B–N, C(1)–N and B–O(1) distances in XII (Table 4) exceed their counterparts in IV by 0.031(5), 0.040(4) and 0.027(4) Å respectively. This bond lengthening might be attributed in part to steric repulsions between the exocyclic substituents. It should be noted in this connection that both the N–B–C and the N–C(1)–C bond angles have been opened at the expense of the O(1)–B–C and S–C(1)–C angles, which are on average 6° smaller.

5. Discussion

The observed [2 + 3] cycloaddition reactions of A with nitrile oxides are, to our knowledge, the first involving aminoboranes to be reported. We point out, however, that some iminoboranes Ar–B=N–Ar have been shown to react analogously with nitrile oxides to

Table 5
Crystal data and refinement details for IV and XII

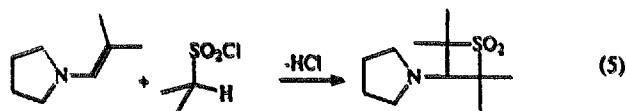
	IV	XII
Formula	C ₉ H ₁₅ BF ₆ N ₂ O	C ₇ H ₁₂ BF ₆ NO ₂ S
<i>M_r</i>	292.0	299.0
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.614(2)	7.8320(6)
<i>b</i> (Å)	13.074(3)	11.314(1)
<i>c</i> (Å)	12.265(3)	14.068(1)
β (°)	103.36(2)	98.165(7)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	1.443	1.610
<i>r</i> (°)	23	22
λ (Å)	0.71073	1.54184
2θ-limits (°)	4–50	2–138.2
Measured reflections	5204	2745
Unique reflections	2367	2301
Observed (<i>F_o</i> ≥ 4σ(<i>F_o</i>))	1752	1946
Monitor correction	1.00–0.89	0.987–1.064
Crystal size (mm ³)	0.38 × 0.44 × 0.49	0.25 × 0.32 × 0.46
μ (mm ⁻¹)	0.11	3.05
Transmission	0.944–0.971	0.377–0.539
<i>R</i> ^a	0.047	0.051
<i>wR</i> ^b	0.049	0.1143
Δρ (e Å ⁻³)	0.22	0.38
Parameters	192	172

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed reflections only.

^b For IV $wR = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ with the sum over the observed reflections, and for XII $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$ with the sum over all reflections.

form five-membered heterocycles [9]. The thermal as well as hydrolytic stabilities of I–V are surprisingly high. Although the cycloadducts VI–XI obtained from the nitrones are less stable than the latter, their stability still significantly exceeds that of the two examples mentioned [4]. Presumably the inductive effect of the two CF₃ groups bonded to boron is responsible for this favorable stabilization.

The reaction of Me₂C=SO₂ with A is indeed unique, not only because the reactions of the unsubstituted and monosubstituted sulfenes H₂C=SO₂, MeHC=SO₂ and PhHC=SO₂ do not lead to tractable products, but also because formation of the five-membered ring in XII suggests a 1,3 dipolar addition of Me₂C=SO₂ to A. To our knowledge, such a reactivity is unprecedented for methylene sulfenes, which are known to undergo [2 + 2] cycloaddition reactions with enamines – the mode of addition indicating δ – C=Sδ + polarity [6]:



That analogous formation of (CF₃)₂B–NMe₂–SO₂–CMe₂ is not observed might be due to steric crowding of the substituents of such a four-membered ring. The

oxygen of the SO₂ group, being sterically less demanding, can coordinate to the Lewis acidic boron atom of A. Thereby an inverse polarity δ + C=S(=O)–Oδ – is created that makes Me₂C=SO₂ suited to enter as 1,3 dipolar species into a [2 + 3] cycloaddition reaction. The sterically less crowded sulfenes RHC=SO₂, with R = Ph, Me, H, might well add to A in the common way, with a δ – C=Sδ + polarization of the C=S bond to form the cyclic sulfonamides (CF₃)₂B–NMe₂–SO₂–CHR in a [2 + 2] cycloaddition reaction. Although a ¹³C NMR spectrum of the reaction mixture obtained from A and MeHC=SO₂ shows a broad signal at 50 ppm which can be ascribed to a carbon atom bonded to boron in a (CF₃)₂B–CHMe–SO₂ fragment, the species giving rise to this resonance could not be identified. Therefore speculation on products and reaction mechanisms seems not to be warranted at present.

6. Experimental

6.1. X-ray structural determination

Crystals of IV and XII grew from their respective chloroform solutions and were mounted in glass capillaries. X-ray measurements on IV were made with a Siemens-AED-1 diffractometer using Zr filtered Mo K α radiation, while data on XII were gathered with a Siemens P3 diffractometer equipped with a Cu tube and a graphite monochromator. Intensities were collected using 2θ–ω scan techniques. Crystal data are listed in Table 5. The structure of IV was solved using the program SHELXS-86 [10] and refined on *F* with SHELX-76

Table 6
Positional and equivalent isotropic displacement parameters (Å²)^a for the non-hydrogen atoms of IV

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
F(1)	1.2017(2)	0.3065(1)	0.2647(1)	0.1072(8)
F(2)	1.1601(2)	0.4319(1)	0.1529(2)	0.1078(8)
F(3)	1.1621(2)	0.4538(2)	0.3266(2)	0.1268(9)
F(4)	0.6693(2)	0.4741(1)	0.1865(2)	0.0998(8)
F(5)	0.8760(2)	0.5558(1)	0.1654(2)	0.1076(8)
F(6)	0.8554(2)	0.5099(1)	0.3299(1)	0.1106(8)
O	0.8837(2)	0.2974(1)	0.2945(1)	0.0670(6)
N(1)	0.8456(2)	0.3106(1)	0.0996(1)	0.0447(6)
N(2)	0.7399(2)	0.2485(1)	0.2419(1)	0.0631(7)
C(1)	0.7120(2)	0.2571(1)	0.1365(2)	0.0462(7)
C(2)	0.5605(3)	0.2144(2)	0.0617(2)	0.0603(9)
C(3)	0.5936(3)	0.1436(2)	–0.0299(2)	0.076(1)
C(4)	0.4765(4)	0.1507(2)	0.1362(3)	0.095(1)
C(5)	0.4484(3)	0.3011(2)	0.0092(3)	0.091(1)
C(6)	0.9567(3)	0.2278(2)	0.0765(2)	0.0651(9)
C(7)	0.8017(3)	0.3766(2)	–0.0027(2)	0.0655(9)
C(8)	1.1114(3)	0.3900(2)	0.2391(2)	0.076(1)
C(9)	0.8292(3)	0.4776(2)	0.2223(2)	0.075(1)
B	0.9205(3)	0.3697(2)	0.2152(2)	0.0542(9)

^a $U_{eq} = \frac{1}{3} \sum_i \sum_j a_i a_j a_i^* a_j^* U_{ij}$.

Table 7
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2)^a for the non-hydrogen atoms of XII

Atom	x	y	z	U_{eq}
S	0.01622(11)	0.20694(6)	0.32094(5)	0.0628(3)
F(1)	-0.0388(3)	0.2807(2)	-0.01656(14)	0.0996(8)
F(2)	-0.1314(3)	0.1500(2)	0.07295(14)	0.0850(6)
F(3)	0.1206(3)	0.1332(2)	0.0348(2)	0.1064(8)
F(4)	0.3708(3)	0.4053(2)	0.1997(2)	0.1167(10)
F(5)	0.3908(3)	0.2478(2)	0.1208(2)	0.1289(11)
F(6)	0.2689(3)	0.4015(2)	0.0517(2)	0.1257(10)
O(1)	0.1339(2)	0.2021(2)	0.23777(14)	0.0560(5)
O(2)	-0.1476(3)	0.1488(2)	0.2900(2)	0.0810(7)
N	-0.0299(3)	0.3858(2)	0.1956(2)	0.0445(5)
C(1)	-0.0207(4)	0.3676(2)	0.3049(2)	0.0585(7)
C(2)	0.0094(5)	0.2125(3)	0.0620(2)	0.0657(8)
C(3)	0.2807(4)	0.3361(3)	0.1332(3)	0.0817(11)
C(4)	-0.2149(3)	0.3716(3)	0.1480(2)	0.0633(8)
C(5)	0.0153(4)	0.5111(2)	0.1723(2)	0.0656(9)
C(6)	-0.1834(6)	0.4024(4)	0.3445(3)	0.0943(13)
C(7)	0.1382(6)	0.4264(3)	0.3608(3)	0.0991(14)
B	0.0971(4)	0.2859(3)	0.1576(2)	0.0494(7)

^a See Table 6.

[11] using only the observed reflections. Structural calculations on XII were made with the SHELXTL program package, refinement being made on F^2 using all unique reflections. In both structures the positions of the methyl hydrogen atoms were idealized with allowance for departure from the staggered conformation. The final coordinates of the non-hydrogen atoms of IV and XII are listed in Tables 6 and 7 respectively [12].

6.2. Preparation of I–XII

6.2.1. 5,5-Bis(trifluoromethyl)-4,4-dimethyl-3-mesityl-1-oxa-2-aza-4-azonia-5-boratacyclopent-2-ene (I)

To a stirred solution of 1.61 g (10 mmol) of MesCNO in 10 ml of CH_2Cl_2 was added dropwise 1.93 g (10 mmol) of $(\text{CF}_3)_2\text{BNMe}_2$ at 0°C. The reaction mixture was then allowed to warm to room temperature as

stirring was continued for 30 min. The solvent and other volatile by-products were removed in vacuo at 0.1 mbar and 20°C and the residue was recrystallized from CHCl_3 . Yield 2.76 g (78%), m.p. 102°C. IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1623 mb; $\nu(\text{CF}_3)$ 1119 vs, 1100 vs, 1097 vs.

6.2.2. 5,5-Bis(trifluoromethyl)-4,4-dimethyl-3-phenyl-1-oxa-2-aza-4-azonia-5-boratacyclopent-2-ene (II), 5,5-bis(trifluoromethyl)-4,4-dimethyl-3-p-chlorophenyl-1-oxa-2-aza-4-azonia-5-boratacyclopent-2-ene (III), 5,5-bis(trifluoromethyl)-4,4-dimethyl-3-t-butyl-1-oxa-2-aza-4-azonia-5-boratacyclopent-2-ene (IV), 5,5-bis(trifluoromethyl)-4,4-dimethyl-3-i-propyl-1-oxa-2-aza-4-azonia-5-boratacyclopent-2-ene (V)

General procedure. To a stirred solution of 8 mmol of the corresponding hydroxamic acid chloride $\text{R}-\text{C}(\text{Cl})=\text{NOH}$ ($\text{R} = \text{Ph}$, $^p\text{C}_6\text{H}_4$, C_6F_5 , ^tBu , ^iPr) in 50 ml ether was added 8 mmol of NEt_3 at -30°C as stirring was continued for 1 h. The reaction mixture was filtered at -30°C; then 8 mmol of $(\text{CF}_3)_2\text{BNMe}_2$ was added dropwise to the filtrate under stirring. The solvent and other volatile by-products were removed at 0.1 mbar and 20°C, and the residue was recrystallized from CHCl_3 .

II (yield 44%), m.p. 86°C. IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1653 m; $\nu(\text{CF}_3)$ 1127 vs, 1102 vs.

III (yield 29%), m.p. 68°C. IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1653 m; $\nu(\text{CF}_3)$ 1104 vs, 1099 vs.

IV (yield 51%), m.p. 135°C. IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1602 w; $\nu(\text{CF}_3)$ 1113 vs, 1094 vs.

V (yield 34%), m.p. 99°C. IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1622 w; $\nu(\text{CF}_3)$ 1108 vs, 1092 vs.

6.2.3. 5,5-Bis(trifluoromethyl)-2,4,4-trimethyl-3-phenyl-1-oxa-2-aza-4-azonia-5-boratacyclopentane (VI), 5,5-bis(trifluoromethyl)-2,4,4-trimethyl-3-p-chlorophenyl-1-oxa-2-aza-4-azonia-5-boratacyclopentane (VII), 5,5-bis(trifluoromethyl)-2,4,4-trimethyl-3-pentafluorophenyl-1-oxa-2-aza-4-azonia-5-boratacyclopentane (VIII), 5,5-bis(trifluoromethyl)-2,4,4-trimethyl-3-t-butyl-1-oxa-

Table 8
Elemental analyses

Compound	Formula	Anal. Found(Calc.) (%)		
		C	H	N
I	$\text{C}_{14}\text{H}_{17}\text{BF}_6\text{N}_2\text{O}$	47.1(47.49)	5.0(4.84)	8.1(7.91)
II	$\text{C}_{11}\text{H}_{11}\text{BF}_6\text{N}_2\text{O}$	41.4(42.34)	3.8(3.55)	8.8(8.98)
III	$\text{C}_{11}\text{H}_{10}\text{BClF}_6\text{N}_2\text{O}$	36.7(38.13)	3.2(2.91)	7.9(8.09)
IV	$\text{C}_9\text{H}_{15}\text{BF}_6\text{N}_2\text{O}$	37.0(37.02)	5.2(5.18)	9.7(9.59)
V	$\text{C}_8\text{H}_{13}\text{BF}_6\text{N}_2\text{O}$	34.6(34.56)	4.6(4.71)	10.1(10.08)
VI	$\text{C}_{12}\text{H}_{13}\text{BF}_6\text{N}_2\text{O}$	43.6(43.93)	4.7(4.61)	8.5(8.54)
VII	$\text{C}_{12}\text{H}_{14}\text{BClF}_6\text{N}_2\text{O}$	39.4(39.76)	3.9(3.89)	7.7(7.73)
VIII	$\text{C}_{12}\text{H}_{10}\text{BF}_{11}\text{N}_2\text{O}$	34.4(34.48)	2.6(2.41)	6.6(6.70)
IX	$\text{C}_{10}\text{H}_{19}\text{BF}_6\text{N}_2\text{O}$	36.9(38.99)	6.1(6.22)	9.0(9.09)
X	$\text{C}_9\text{H}_{17}\text{BF}_6\text{N}_2\text{O}$	36.9(36.76)	6.1(5.83)	8.9(9.52)
XII	$\text{C}_7\text{H}_{12}\text{BF}_6\text{NO}_2\text{S}$	28.0(28.12)	4.0(4.04)	4.6(4.68)

2-aza-4-azonia-5-boratacyclopentane (IX), 5,5-bis(trifluoromethyl)-2,4,4-trimethyl-3-*i*-propyl-1-oxa-2-aza-4-azonia-5-boratacyclopentane (X), 5,5-bis(trifluoromethyl)-4,4-dimethyl-2,3-diphenyl-1-oxa-2-aza-4-azonia-5-boratacyclopentane (XI)

General procedure. To a stirred solution of 10 mmol of the respective nitron in 30 ml of pentane was added dropwise 10 mmol of $(CF_3)_2BNMe_2$ at $-10^\circ C$. The cycloadducts VI–XI precipitated and were recrystallized from dry $CHCl_3$.

VI (yield 80%), dec. $\sim 105^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1103 vs, 1088 vs.

VII (yield 76%), dec. $\sim 100^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1110 vs, 1105 vs.

VIII (yield 67%), dec. $\sim 94^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1090 sb.

IX (yield 75%), dec. $\sim 71^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1099 sb.

X (yield 73%), dec. $\sim 71^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1099 sb.

XI (yield 73%), dec. $\sim 81^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1095 sb.

6.2.4. 5,5-Bis(trifluoromethyl)-3,3,4,4-tetramethyl-1-oxa-2-thia-4-azonia-5-boratacyclopentane-2-oxide (XII)

To a stirred solution of 15 mmol of triethylamine and 10 mmol of $(CF_3)_2BNMe_2$ in 30 ml of dry ether was added dropwise 10 mmol of 1PrSO_2Cl at $0^\circ C$. Stirring was continued for 30 min, and all the volatile material removed in vacuo at $20^\circ C$. The residue was suspended in 30 ml of $CHCl_3$, and the ammonium salt removed by extraction with three 10 ml portions of water. The solvent $CHCl_3$ was evaporated in vacuo and **XI** sublimed at 0.1 mbar and $80^\circ C$. Yield (63%).

XII, m.p. $130^\circ C$. IR (cm^{-1}): $\nu(CF_3)$ 1124 vs, 1089 vs; $\nu(S=O)$ 1002 s.

For elemental analyses see Table 8.

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