On the reaction of dimethylamino-bis(trifluoromethyl)borane with sulphenes [1]

Gottfried Pawelke

Anorganische Chemie, Fachbereich 9, Universität-Gesamthochschule, D-42097 Wuppertal, Germany

Abstract

Dimethylamino-bis(trifluoromethyl)borane ($(CF_3)_2BNMe_2$) reacted at -10 °C with sulphenes ($RHC=SO_2$) to form unstable adducts, which were hydrolysed by water buffered with $KHCO_3$ to yield the stable salts $K[O_3S–CRH–B(CF_3)_2–NHMe_2]$ ($R \equiv H$ (**1**), Me (**2**) and Et (**3**)). © 1997 Elsevier Science S.A.

1. Introduction

In a preceding contribution, we reported the [2 + 3] cycloaddition reactions of dimethylamino-bis(trifluoromethyl)borane [1]. During the course of these studies, we found that the sulphene $Me_2C=SO_2$ acts, somewhat unexpectedly, as a 1,3 dipole and readily forms a five-membered heterocycle ($(CF_3)_2\overline{B-NMe_2-CMe_2-S(=O)-O}$) with $(CF_3)_2$-$BNMe_2$. The composition of this [2 + 3] cycloaddition product was proven by X-ray structural analysis. In contrast, initial attempts to react less substituted sulphenes $RHC=SO_2$ ($R \equiv H$, Me, Et) with the aminoborane yielded black, tarry material that could not be characterized. This unsatisfactory result stimulated us to investigate the reaction of sulphenes with $(CF_3)_2BNMe_2$ in more detail.

2. Results and discussion

Sulphenes, such as $RHC=SO_2$ ($R \equiv H$, Me, Et), are unstable species, which are generated in situ by the abstraction of HCl from the corresponding alkylsulphonyl chlorides RCH_2SO_2Cl using triethylamine. They are known to be typical 1,2 dipoles with a negatively polarized carbon atom and a positively polarized sulphur atom [2]. Therefore it has been speculated that these sulphenes may add to $(CF_3)_2BNMe_2$ in a [2 + 2] cycloaddition reaction to form the four-membered heterocycle $(CF_3)_2\overline{B-NMe_2-SO_2-CHR}$ (Scheme 1).

Scheme 1.
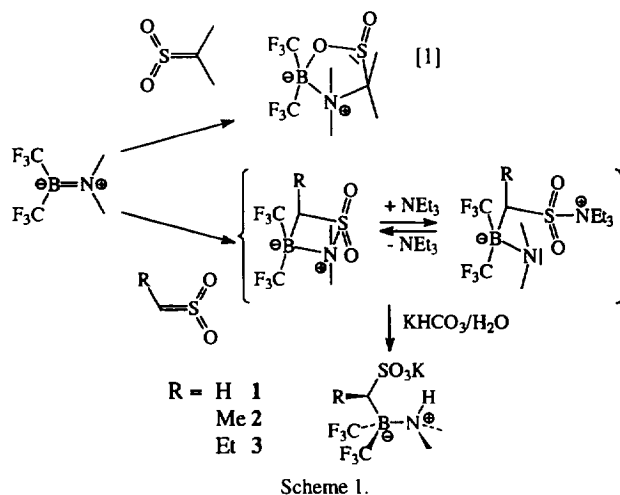
These four-membered rings are obviously unstable at room temperature; their instability is due to the existence of two electrophilic centres, sulphur and boron, in the ring which compete for saturation. Such heterocycles may be described as cyclic sulphonamides, and it is known that the nitrogen in a sulphonamide is a poor donor. Due to the presence of excess triethylamine in the reaction mixture, these rings could enter into an equilibrium with acyclic adducts (Scheme 1). Therefore we have tried to trap these intermediates and transfer them into more stable derivatives. This was achieved by adding water buffered with $KHCO_3$ to the reaction mixture. Thus we obtained the stable salts $K[O_3S–CRH–B(CF_3)_2–NHMe_2]$ ($R \equiv H$ (**1**), Me (**2**) and Et (**3**)) (Scheme 1). This experimental result does not provide absolute proof for the

Table 1
NMR spectral data for 1–3 (δ in ppm, J in Hz)[a]

	1	2	3
^{1}H			
δ (NCH_3)	2.91	2.86	2.86
		2.92	2.90
δ (CCH_3)		1.50, d, ^3J(HH) 8.1	1.23, t, ^3J(HH) 7.6
δ (CCH_2)			~1.95
			~1.99
δ (BCH_n)	2.78	2.78	2.51
^{19}F			
δ (CF_3)	−62.2	−59.3	−59.4
		−60.4	−59.5
^{11}B			
δ (B)	−7.6	−7.5	−7.3
^{13}C			
δ (NCH_3)	39.80, sept., ^4J(CF) 2.5	39.26	41.18
		39.88, sept., ^4J(CF) 2.5	41.74, sept., ^4J(CF) 2.3
δ (CCH_3)		11.30	17.33
δ (CCH_2)			21.92, sept., ^4J(CF) 1.9
δ (BCH_n)	40.0	45.6	55.5

[a] In D_2O. ^{1}H: 400.13 MHz, internal standard HOD = 4.80 ppm. ^{19}F: 376.46 MHz, external standard CFCl$_3$. ^{11}B: 80.25 MHz, external standard BF$_3$·OEt$_2$. ^{13}C: 100.63 MHz, external standard tetramethylsilane (TMS).

existence of the proposed four-membered ring or for the open chain species as an intermediate. However, it shows that this particle contains at least a third carbon–boron bond linking the sulphonate residue to boron.

The NMR chemical shifts and coupling constants, which are set out in Table 1, are consistent with the proposed structure, and only a few comments are necessary. As usual, the resonances of the CF$_3$ groups were not found in the ^{13}C NMR spectra due to quadrupole broadening by the boron nucleus, but the broad signals of the sulphonate carbon atoms demonstrate the existence of the B–C–S framework in 1–3. The asymmetric carbon atom of 2 and 3 causes splitting of the BCF$_3$ (^{19}F), NCH$_3$ (^{1}H) and NCH$_3$ (^{13}C) resonances, and one of the latter is split into septets by a ^4J(CF) coupling.

The molecular masses of 1–3 were determined by ESI/ neg. spectra (CH$_3$CN–H$_2$O) which showed the mole peaks of the anions [O$_3$S–CHR–B(CF$_3$)$_2$–NHMe$_2$]$^-$ (100%) and the cluster peaks [K$_2$[O$_3$S–CHR–B(CF$_3$)$_2$–NHMe$_2$]$_3$]$^-$ (approximately 3%).

To our knowledge, compounds 1–3 are the first species with an N–B–C–SO$_3$ framework. The inertness of the boron–nitrogen bond in these novel organoborates is remarkable. Compounds 1–3 are thermally stable up to approximately 200 °C and stable in water over the pH range 1–14. This must be ascribed to the strong electron withdrawing effect of the two CF$_3$ groups, providing the boron species with chemical and physical properties which differ dramatically from those of the non-fluorinated analogues [3] and, in many cases, stabilize new organoboron compounds with tetracoordinated boron.

3. Experimental details

3.1. Potassium-2,2-bis(trifluoromethyl)-3-methyl-3-azonia-2-borata-butanesulphonate (1), potassium-2,2-bis(trifluoromethyl)-1,3-dimethyl-3-azonia-2-borata-butanesulphonate (2) and potassium-2,2-bis(trifluoromethyl)-1-ethyl-3-methyl-3-azonia-2-borata-butanesulphonate (3)

To a stirred solution (10 mmol) of (CF$_3$)$_2$BNMe$_2$ and 25 ml of triethylamine in 30 ml of dry ether (10 mmol), methane-, ethane- or propane-sulphonyl chloride was added dropwise at −30 °C. The reaction mixture was stirred and allowed to warm to approximately 0–5 °C in about 30 min when NHEt$_3$Cl was formed. The reaction mixture was cooled to approximately 0 °C and 50 ml of a saturated KHCO$_3$ solution was added with stirring leading to the precipitation of 1–3. The products were filtered, washed with 2–3 ml of ether and H$_2$O and crystallized from H$_2$O; 1 and 3 gave a monohydrate and 2 formed a dihydrate. Yields: 1, 82%; 2, 78%; 3, 52%.

K[O$_3$S–CH$_2$–B(CF$_3$)$_2$–NHMe$_2$] · H$_2$O: Raman (cm^{-1}): 1047 vs, ν(SO$_3$); 710 vs, δ_s(CF$_3$).

M = 345.11   (C$_5$H$_{11}$BF$_6$KNO$_4$S)
Calculated (%)   C, 17.40; H, 3.21; N, 4.06
Found (%)   C, 16.94; H, 2.93; N, 3.72

On heating from 48 to 104 °C, 5.2% loss of weight took place which, within experimental error, corresponds to one molecule of H$_2$O (calculated, 5.22%).

K[O$_3$S–CH(CH$_3$)–B(CF$_3$)$_2$–NHMe$_2$] · 2H$_2$O: Raman (cm^{-1}): 1042/1059 vs, ν(SO$_3$); 716 vs, δ_s(CF$_3$).

$M = 377.15$ $(C_6H_{15}BF_6KNO_5S)$
Calculated (%)   C, 19.11; H, 4.01; N, 3.71
Found (%)   C, 19.14; H, 3.87; N, 3.81

On heating from 40 to 130 °C, 9.5% loss of weight took place which, within experimental error, corresponds to two molecules of H_2O (calculated, 9.55%).

$K[O_3S-CH(CH_2CH_3)-B(CF_3)_2-NHMe_2] \cdot H_2O$: Raman (cm^{-1}): 1037 vs, $\nu(SO_3)$; 720 vs, $\delta_s(CF_3)$.

$M = 373.16$ $(C_7H_{15}BF_6KNO_4S)$
Calculated (%)   C, 22.53; H, 4.05; N, 3.75
Found (%)   C, 22.36; H, 3.86; N, 3.50

On heating from 34 to 110 °C, 4.8% loss of weight took place which, within experimental error, corresponds to one molecule of H_2O (calculated, 4.77%).

Acknowledgements

References

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