B-ALKYLATION OF DIMETHYLAMINO-BIS(TRIFLUOROMETHYL)BORANE BY 1-ALKYNES

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Abstract

Dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (**A**), is alkylated by 1-alkynes, H-C≡C-R, in three different ways. Alkynes with R = Ph, *p*-Tol, and -C≡CH-$(CH_2)_3$-CH$_2$ react exclusively via the hydride transfer route (a) to yield the corresponding methylmethyleneimine stabilized adducts (*trans*-R-CH=CH)$(CF_3)_2B{\cdot}N(=CH_2)Me$ (**Ia**), (**IIa**), and (**IIIa**). For R = $SiMe_3$ the occurrence of two reactions leads to formation of a 6:4 mixture of (*trans*-Me_3Si-CH=CH)$(CF_3)_2B{\cdot}N(=CH_2)Me$) (**IVa**) which is formed by hydride transfer, and (Me_3Si-C≡C)$(CF_3)_2B{\cdot}NHMe_2$ (**IVb**), which results from C-H addition (**b**) across the B=N double bond of **A**. On the other hand, reactions with alkynes possessing at least one hydrogen atom attached to the α carbon of the R group yielded ca. 7:3 mixtures of (*trans*-R^1R^2HC-CH=CH)$(CF_3)_2B{\cdot}N(=CH_2)Me$ resulting from the hydride transfer reaction, and (R^1R^2C=C=CH)$(CF_3)_2B{\cdot}NHMe_2$ (R^1,R^2 = $(CH_2)_5$ (**Va/c**); R^1 = H, R^2 = *n*-C_3H_7 (**VIa/c**) and R^1 = H, R^2 = *n*-C_4H_9 (**VIIa/c**)) which are products of an ene-type reaction (**c**). The novel boranes have been characterized by elemental analyses, multinuclear NMR, IR and mass spectroscopy.

Introduction

In a preceding paper we have reported on alkylation of the boron atom of dimethylaminobis-(trifluoromethyl)borane (**A**) by 1-alkenes [1]. Depending on the kind of substitution at the double bond, two different types of reaction were observed. Alkenes of the general formula H_2C=CHR, with substituents R lacking a hydrogen atom α to the C=C bond, undergo a hydride shift reaction to yield methylmethyleneimine stabilized boranes $(RCH_2CH_2)(CF_3)_2B{\cdot}N(=CH_2)Me$ (eqn. (1)):

$$(CF_3)_2BNMe_2 + H_2C{=}CHR \rightarrow (RCH_2CH_2)(CF_3)_2B{\cdot}N(=CH_2)Me \qquad (1)$$

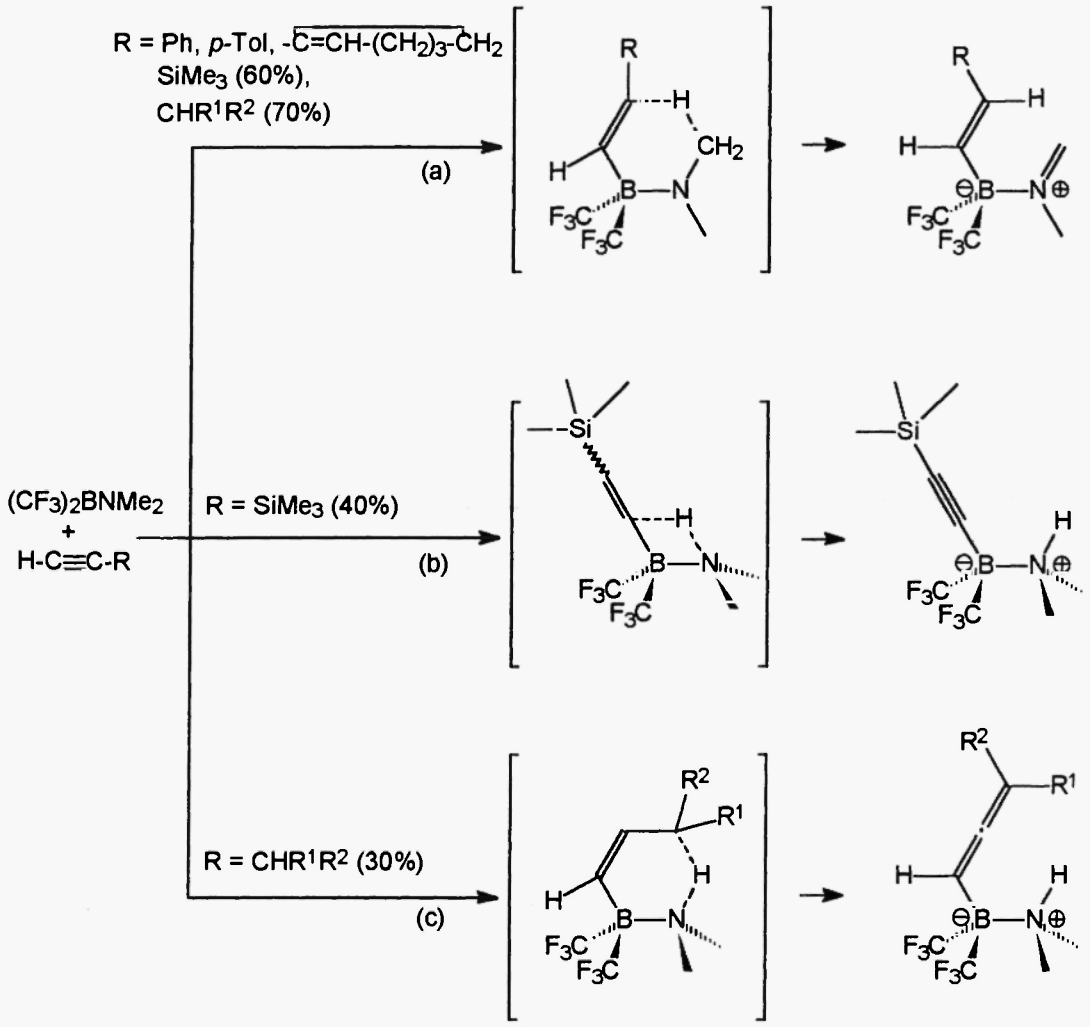
To the contrary, alkenes of the general formula $H_2C{=}C(CH_3)R$ reacted preferentially in an ene-type reaction to form the dimethylamine stabilized boranes $(RC(=CH_2)CH_2)(CF_3)_2B{\cdot}NHMe_2$ (eqn. (2)):

$$(CF_3)_2BNMe_2 + H_2C{=}C(CH_3)R \rightarrow (RC(=CH_2)CH_2)(CF_3)_2B{\cdot}NHMe_2 \qquad (2)$$

This selective behaviour and the observation that *t*-Bu-C≡C-H formed exclusively (*trans*-*t*-Bu-CH=CH)$(CF_3)_2B{\cdot}N(=CH_2)Me$ [2] when reacted with **A** prompted us to investigate reactions of **A** with terminal alkynes H-C≡C-R more thoroughly. We were particularly curious about the influence of R. Therefore this substituent was varied in a systematic fashion. Here we report on our results.

Results and Discussion

The 1-alkynes H-C≡C-R which we have reacted with the aminoborane **A** belong to two classes. The first group comprises alkynes not disposing over a hydrogen atom in the α position of the substituent R (e.g. R = Ph, *p*-Tol, -C=CH-$(CH_2)_3$-CH_2 , Me_3Si). Alkynes of the second group bear at least one such hydrogen atom (i.e., R = CHR^1R^2). The reactions which **A** underwent with these two different types of alkynes are displayed in Scheme 1.



Scheme 1: Reactions of 1-alkynes with $(CF_3)_2BNMe_2$.

We have found that phenylethyne, *p*-tolylethyne and 1-ethynyl-1-cyclohexene, which belong to the first group, reacted exclusively according to the hydride shift route (**a**) to yield the respective methylmethyleneimine stabilized trifluoromethylboranes. We assume that in a first step the alkyne coordinates to boron and then the hydrogen is transferred from the nitrogen-bonded methyl group to the β carbon atom of the alkyne. A six-membered cyclic transition state may be involved. In this

context it should be mentioned that only primary alkynes react with **A** ; secondary alkynes, e.g. 2-butyne, were found to be unreactive. This suggests that coordination of boron by the α-acetylenic carbon initiates all reactions of **A** with alkynes.

To our surprise, trimethylsilylethyne was found to give a mixture when reacted with **A**. While this mixture contained 60 % of a product (**IVa**) formed according to pathway a, 40 % (**IVb**) resulted from an addition of the C-H link to the B=N double bond (eqn. b). The reason for this behaviour is neither the acidity of the C-H bond nor the steric strain exerted by the trimethylsilyl group because *t*-Bu-C≡C-H was found to react exclusively according to pathway (a) [2]. Obviously the silyl group destabilizes electronically the carbo-cationic center. Hereby reaction pathway b is favoured. Alkynes H-C≡C-R with a substituent R = CHR^1R^2 were found to prefer pathway a, but at room temperature about 30 % underwent an ene-type reaction (**c**) to yield dimethylamine-stabilized bis(trifluoromethyl)boranes $(R^1R^2C{=}C{=}CH)(CF_3)_2B{\cdot}NHMe_2$ (R^1,R^2 = $(CH_2)_5$ (**Va/c**); R^1 = H, R^2 = *n*-C_3H_7 (**VIa/c**) and R^1 = H, R^2 = *n*-C_4H_9 (**VIIa/c**) with an allenic residue bond to the boron atom. The isomer distribution **a/c** is temperature dependent. When the reaction of **A** and 1-pentyne is carried out at about 2 °C rather than at 20 °C, the amount of **VIa** increases to 90 %. However, pure **VIa** could not be obtained because further lowering of the temperature essentially brought the reaction to a halt.

The observed hydride shift and ene-type reactions of **A** with 1-alkynes are unprecedented in aminoborane chemistry. Their occurrence is made possible by the strong electron withdrawal of the two CF_3 groups attached to boron. The formation of **IVb** is related to a reaction reported by Schweizer [3] of $B(NMe_2)_3$ with phenylethyne which gave Ph-C≡C-$B(NMe_2)_2$ according to eqn. (3). However, here boron remains three coordinate. No analogous elimination of dimethylamine

$$Ph\text{-}C{\equiv}C\text{-}H + B(NMe_2)_3 \xrightarrow{140\ °C} Ph\text{-}C{\equiv}C\text{-}B(NMe_2)_2 + HNMe_2 \qquad (3)$$

occurs for **IVb**. The BN bond in amine boranes is notably stronger than in analogous alkyl derivatives when boron carries trifluoromethyl groups. Breaking this bond in **IVb** would lead to extensive degradation of the CF_3 groups because hitherto unknown donor-free trifluoromethyl boranes $(CF_3)_2BR$ (R = aryl, alkyl, alkenyl, alkynyl) would be formed. These are expected to decompose rapidly by elimination of difluorocarbene.

Properties and spectra

All novel boranes are colourless solids, or oily liquids. Attempts to separate the isomers in mixtures of **IV** to **VII** by distillation were unsuccessful. **Warning:** Methylmethyleneimine stabilized adducts of bis(trifluoromethyl)borane derivatives may decompose explosively when heated to 90 °C. Compounds **IVb**, **Vc**, **VIc** and **VIIc** are stable to air and moisture while species containing a methylmethyleneimino group readily undergo hydrolysis to give the corresponding methylamine adducts according to eqn. (4)

$$R(CF_3)_2B{\cdot}N(=CH_2)Me \xrightarrow[-\ OCH_2]{+\ H_2O} R(CF_3)_2B{\cdot}NH_2Me \qquad (4)$$

TABLE 1: NMR spectral data for **Ia - VIIc** (δ in ppm)[a]

^1H	**Ia**	**IIa**	**IIIa**	**IVa**	**IVb**	**Va**	**Vc**	**VIa**	**VIc**	**VIIa**	**VIIc**
δ (BC*H*=C*H*)	6.27 6.90	6.31 6.96	5.49 6.48	6.28 6.41		5.38 5.93	4.77	5.42 5.97		5.42 5.99	
δ (BC*H*CC*H*)							4.76		4.92 5.01		4.86 4.96
δ (CC*H*=)			5.79								
δ (NH(CH_3)$_2$)					2.87		2.80		2.82		2.81
δ (N*H*)					~4.2		~4.2		~4.2		~4.2
δ (-CH_2-)			~1.66 ~2.16			~1.1	~1.1 ~1.3	1.43 2.09	2.02	~1.36 ~1.38	~1.37 1.98
δ (-C*H*-)						1.98	~1.7			2.12	
δ (NCH_3)	3.66	3.65	3.67	3.68		3.65		3.65		3.64	
δ (N=CH_2)	7.60 7.78	7.51 7.75	7.80 7.84	7.70 7.80		7.70 7.82		7.70 7.82		7.70 7.80	
δ (C-CH_3)		2.45						0.90	1.02	0.91	0.95
δ (C$_6$*H*$_5$)	7.24 7.50	7.25 7.47									
δ (Si(CH_3)$_3$)				0.07	0.17						
^{19}F											
δ (CF_3)	-65.3	-64.4	-65.3	-65.5	-64.0	-66.5	-56.7	-65.3	-64.3	-65.2	-64.2
^{11}B											
δ (*B*)	-6.2	-7.6	-7.7	-8.0	-12.5	-7.7		-7.3		-8.0	
^{13}C											
δ (BCH=)	~126	~125	~121	~146		~123	~79	~127	~82	~126	~82
δ (C*C*H=)	141.7	141.4	137.2	146.7		150.3	98.8	144.6	89.1	144.7	87.1
δ (Si*C*H=)			130.6 145.7								
δ (C-*C*H$_3$)		20.9						13.5	13.5	13.5	13.4
δ (N=*C*H$_2$)	168.5	168.8	168.4	167.9		168.3		168.5		168.7	
δ (NCH$_3$)	48.3	48.0	48.3	48.5		48.1		48.2		48.0	
δ (NH(CH$_3$)$_2$)					40.8		40.3		40.3		40.3
δ (Si(CH$_3$)$_3$)				-1.6	-0.1						
δ (-*C*H-)						43.6					
δ (-CH$_2$-)			22.6 22.7 24.2 26.0			25.9 26.1 32.6	26.0 27.4 30.6	22.1 38.3	21.1	22.2 31.1 35.9	30.2 22.7
δ (C=*C*=C)							202.7		206.8		207.4
δ (R-*C*≡CB)					~108						
δ (C$_6$H$_5$)	126.3 128.6 127.9 138.3	126.1 129.3 135.6 137.8									

[a] **Ia - VIIc** in $CDCl_3$. ^1H: 250.13 MHz, int. std. $CHCl_3$ = 7.27 ppm. ^{13}C: 62.9 MHz, int. std. $CDCl_3$ = 77.0 ppm. ^{19}F: 84.67 and 235.37 MHz, int. std. $CFCl_3$. ^{11}B: 25.52 and 79.79 MHz. ext. std. BF_3 OEt_2.

The ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **Ia - VIIa/c** have been recorded. The ^{1}H and ^{13}C NMR parameters, which are set out in TABLE 1, reveal significant differences between the three structural isomers (a), (b) and (c). The *trans* arrangement at the C=C double bond in type a compounds is established by the large coupling constant ^{3}J (HH) = 18 - 19 Hz. A singlet in the ^{1}H NMR spectrum at 3.65 ppm indicates the presence of a C=NCH_3 group while the N=CH_2 link appears as an AB spin system at 7 - 8 ppm with ^{2}J (HH) ~11 Hz . In the ^{13}C spectra the corresponding imino atom resonance N=CH_2 appears at 167 ppm. The allenic system in compounds of type c is clearly indicated by ^{13}C resonances at 207 (C=*C*=C) and 82 ppm (C=C=*C*-B). Of the two acetylenic carbon atoms in **IVb**, only that in β position (-*C*≡C-B , 108 ppm) was detected. In bis(trifluoromethyl)boranes, alkyne C atoms directly attached to boron appear at 80 ppm, but the signals are extremely broadened and hardly detectable in spectra run under standard conditions. As usual, the CF_3 groups were not found in the ^{13}C NMR spectra due to quadrupole broadening by the boron nucleus. ^{13}C NMR spectra of **VI** and **VII** show some additional very weak signals (not included in TABLE 1), which are tentatively assigned to compounds **VIb** and **VIIb** respectively. Of these resonances a broadened signal at 102 ppm may be ascribed to the R-*C*≡C-B atom.

Some diagnostic infrared and Raman wavenumbers are quoted in the Experimental Part. EI mass spectral data are reported in TABLE 2. In trifluoromethylboron compounds peaks of the molecular ion $[M]^+$ are usually of low intensity, if at all detectable. Compounds **Ia - IIIa** are notable exceptions which give rise to intense $[M]^+$ peaks while in other cases the fragments $[M\text{-}CF_3]^+$ or $[M\text{-}C_2F_5]^+$ usually confirm the molecular weight.

TABLE 2: Selected EI mass spectral data in the order of decreasing intensity (*m/e* (relative intensity (%)) [fragment]$^+$) for compounds **Ia - VIIa/c** .

Ia	176(100)$[M\text{-}C_2F_5]^+$ / 183(58)$[M\text{-}CF_3\text{-}C_2H_5N]^+$ / 115(53)$[C_8H_8B]^+$ / 295(53)$[M]^+$ / 92(31)$[F_2BN{=}CH_2CH_3]^+$ / 226(8)$[M\text{-}CF_3]^+$
IIa	309(100)$[M]^+$ / 190(82)$[M\text{-}C_2F_5]^+$ / 197(64)$[M\text{-}CF_3\text{-}C_2H_5N]^+$ / 129(47)$[C_9H_{10}B]^+$ / 92(19)$[F_2BN{=}CH_2CH_3]^+$ / 240(5)$[M\text{-}CF_3]^+$
IIIa	107(100)$[C_8H_{11}]^+$ / 92(50)$[F_2BN{=}CH_2CH_3]^+$ / 299(32)$[M]^+$ / 180(30)$[M\text{-}C_2F_5]^+$ / 230(2)$[M\text{-}CF_3]^+$
IVa/b	92(100)$[F_2BN{=}CH_2CH_3]^+$ / 94(15)$[F_2BNH(CH_3)_2]^+$ / 73(14)$[(CH_3)_3Si]^+$ / 172(7)$[M\text{-}C_2F_5]^+$ / 98(9)$[(CH_3)_3SiCCH]^+$ / 222(6)$[M\text{-}CF_3]^+$ / 291(1)$[M]^+$
Va/c	109(100)$[C_8H_{13}]^+$ / 94(73)$[C_7H_{10}]^+$ / 67(63)$[C_5H_7]^+$ / 92(34)$[F_2BN{=}CH_2CH_3]^+$ / 301(19)$[M]^+$ / 182(17)$[M\text{-}C_2F_5]^+$ / 232(3)$[M\text{-}CF_3]^+$
VIa/c	92(100)$[F_2BN{=}CH_2CH_3]^+$ / 142(58)$[M\text{-}C_2F_5]^+$ / 100(19)$[M\text{-}C_2F_5\text{-}C_3H_6]^+$ / 192(14)$[M\text{-}CF_3]^+$ / 261(8)$[M]^+$
VIIa/c	92(100)$[F_2BN{=}CH_2CH_3]^+$ / 156(37)$[M\text{-}C_2F_5]^+$ / 114(12)$[M\text{-}C_2F_5\text{-}C_3H_6]^+$ / 247(5)$[M\text{-}C_2H_4]^+$ / 233(5)$[M\text{-}C_4H_8]^+$ / 275(3)$[M]^+$ / 206(5)$[M\text{-}CF_3]^+$

Experimental Part

General procedure:

To a stirred solution of 12 mmol of an alkyne in 20 ml of dry pentane, 2.0 g (10.4 mmol) of $(CF_3)_2BNMe_2$ was added dropwise at 4°C. The mixture was allowed to warm to room temperature, with stirring continued for 4 h. The solvent and other volatile by-products were removed in vacuo at ambient temperature, and the residue was purified by sublimation or distillation in vacuo (40 - 90 °C / $\sim 10^{-1}$mbar) as appropriate. Yields: **Ia** 94% Mp 78 °C; **IIa** 90% Mp. 55 °C; **IIIa** 92 %; **IVa/b** 81 %; **Va/c** 94 %; **VIa/c** 91 %; **VIIa/c** 86 %.

Warning: Compound **IIIa/c** exploded when heated to 100°C in vacuo. No distillation should be attempted. For elemental analyses see TABLE 3.

IR{Ra} cm^{-1} :

Ia 1668 m ν(N=C), 1628 m ν(C=C), 1090 vs ν(CF)

IIa 1664 m ν(N=C), 1622 m ν(C=C), 1090 vs ν(CF)

IIIa 1665 m ν(N=C), 1637 m, 1604 m ν(C=C), 1092 vs ν(CF)

IVa 1665 m ν(N=C), {1591 m }ν(C=C), 1088 vs ν(CF)

IVb 3280 m ν(NH), {2152 m } ν(C≡C)

Va 1662 m ν(N=C), 1633 m ν(C=C), 1090 vsb ν(CF)

Vc 3313w, 3280 m ν(NH), 1952 m ν_{as}(C=C=C), 1090 vsb ν(CF)

VIa 1666 m ν(N=C), 1640 m ν(C=C), 1090 vsb ν(CF)

VIc 3318w, 3279 m ν(NH), 1949 m ν_{as}(C=C=C), 1090 vsb ν(CF)

VIIa 1665 m ν(N=C), 1640 m ν(C=C), 1090 vsb ν(CF)

VIIc 3318w, 3280 m ν(NH), 1947 m ν_{as}(C=C=C), 1090 vsb ν(CF)

TABLE 3: Elemental analyses of **Ia - VIIa/c**

	Formula	found/(calc.)%			
		C	H	N	F
Ia	$C_{12}H_{12}BF_6N$	48.76/(48.85)	4.27/(4.10)		38.2/(38.64)
IIa	$C_{13}H_{14}BF_6N$	50.44/(50.52)	4.51/(4.57)		36.6/(36.88)
IIIa	$C_{12}H_{16}BF_6N$	47.93/(48.19)	5.26/(5.39)	4.49/(4.68)	
IVa/b	$C_9H_{16}BF_6NSi$	36.90/(37.13)	5.42/(5.54)		39.2/(39.16)
Va/c	$C_{12}H_{18}BF_6N$	47.74/(47.87)	6.06/(6.03)		37.6/(37.86)
VIa/c	$C_9H_{14}BF_6N$	40.81/(41.41)	5.29/(5.41)		42.7/(43.67)
VIIa/c	$C_{10}H_{16}BF_6N$	43.78/(43.67)	5.74/(5.86)		41.8/(41.44)

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