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Mendeleev Commun., 2007, **17**, 271–273
Mendeleev Communications

Reactions of boron trifluoride with allylic boranes and 1-boraadamantane

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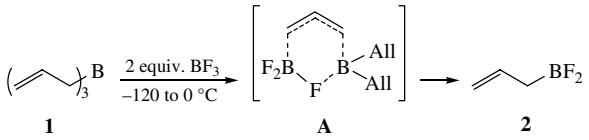
DOI: 10.1016/j.mencom.2007.09.007

The reactions of boron trifluoride with triallyl- and allyldialkylboranes represent a convenient non-catalytic approach to allyl(difluoro)boranes. The rupture of 1-boraadamantane core with BF_3 leads to 3-fluoro-7-difluoroborylmethyl-3-borabicyclo-[3.3.1]nonane derivatives.

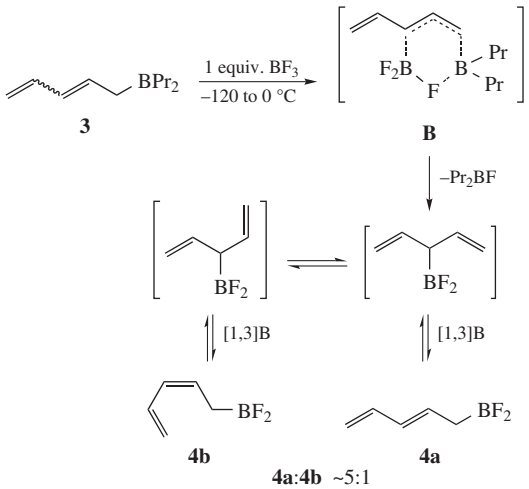
The chemistry of organyl(trifluoro)borates $[RBF_3]M$ (M = K, R'_4N; R = alkyl, aryl, alkenyl, alkynyl, allyl or benzyl) have been extensively studied in the last decade because of their high reactivity and simplicity of preparation in a pure state, *e.g.*, by the interaction of $RB(OH)_2$ and KHF_2.[1] On the other hand, there are only two general approaches to the synthesis of parent organyl(difluoro)boranes: (*1*) the redistribution reaction of trialkylboranes with boron trifluoride in the presence of catalytic amounts of boron hydrides[2] and (*2*) thermal reactions of trialkylboranes with BF_3 etherate at 200 °C[3] when dissociation of R_3B into R_2BH and alkene takes place.



1 A 2

Scheme 1

Recently, it was shown that allyl(dichloro)boranes and allyl(dibromo)boranes, which are highly reactive allylborating reagents,[4–7] can be easily generated *in situ* by the transmetallation of allylic tins with BX_3 (X = F, Cl, Br)[8,9] or, environmentally friendly, by the redistribution reaction of triallylboranes and BCl_3 or BBr_3 in inert solvents (without a B–H catalyst).[6,7]



Scheme 2

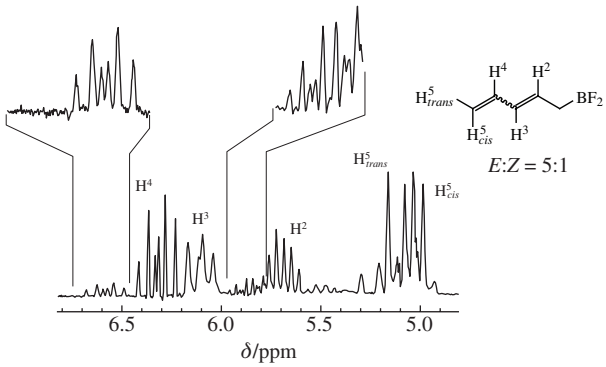


Figure 1 Section plot of the ^1H NMR spectrum of the reaction mixture of 2,4-pentadienyldipropylborane **3** with BF_3 (200.13 MHz, $CDCl_3$) (olefin region).

We have found that triallyl- and allyldialkylboranes readily react with BF_3 at –120 to –100 °C also in the absence of a B–H catalyst, giving rise to the corresponding allyl(difluoro)boranes in almost quantitative yields.

The reaction of boron trifluoride with triallylborane in a 2:1 molar ratio gave rise to allyl(difluoro)borane **2** (Scheme 1),[†] isolated by distillation as a fluid extremely flammable on contact with air. Note that allyl(difluoro)borane, $AllBF_2$, is a compound stable in an inert atmosphere and does not degrade in storage for long periods (months), though the half-life of allyl(difluoro)borane prepared from All_4Sn[9] is 18 h.

A similar reaction with 2,4-pentadienyldipropylborane **3** afforded a mixture of 2,4-pentadienyl(difluoro)borane **4** and dipropylfluoroborane (Scheme 2). Proximity of boiling points

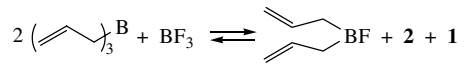
[†] *General procedure for generation of allyl(fluoro)boranes*. All manipulations with organoboron compounds were carried out under dry argon. In a Schlenk tube fitted with a cold trap (–78 °C) and containing allylic borane, a calculated quantity of boron trifluoride was condensed at –120 °C. After stirring for 30 min, the reaction mixture was slowly warmed to 0 °C and monitored by NMR spectroscopy. The products were isolated by distillation from the reaction vessel.

For **2**: 90% yield; bp 4 °C. ^1H NMR (200.13 MHz, $CDCl_3$) δ: 1.95 [br. s, 2H, H(1)], 5.05 [d, 1H, $H(3)_{cis}$, $^3J_{H(3)_{cis}–H(2)}$ 10.0 Hz], 5.09 [d, 1H, $H(3)_{trans}$, $^3J_{H(3)_{trans}–H(2)}$ 17.1 Hz], 5.80 [ddt, 1H, H(2), $^3J_{H(2)–H(3)_{trans}}$ 17.1 Hz, $^3J_{H(2)–H(3)_{cis}}$ 10.0 Hz, $^3J_{H(2)–H(1)}$ 7.3 Hz]. ^{13}C-{^1H} NMR (50.32 MHz, $CDCl_3$) δ: 15–21 (very br., CB), 117.1 [C(3)], 130.1 [C(2)]. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ: 28.0 (t, $^1J_{^{11}B–^{19}F}$ 70 Hz). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: –73.2 (q, $^1J_{^{19}F–^{11}B}$ 70 Hz).

did not allow us to isolate compound **4** in a pure state; however, it was characterised by multinuclear NMR spectroscopy.‡ The ^{1}H NMR spectrum of **4** shown in Figure 1 clearly indicates the presence of *E*- and *Z*-isomers **4a** and **4b** in a ~5:1 ratio.

The values $^3J_{H(2)–H(3)}$ 14.9 Hz for **4a** and 10.0 Hz for **4b** point out the predominance of the *E*-isomer in the reaction mixture.

The transfer of allylic groups from one boron atom (in **1** or **3**) to another (in BF_3) occurs with allylic rearrangement *via* a six-membered transition state like **A** or **B**. This was previously demonstrated by investigating the exchange reactions of tricrotylborane with BX_3 (X = Cl, OR or SR).[10,11]



1 **5**

5:**2**:**1** ~1:1:2

Scheme 3

The methodology proposed is inapplicable to the preparation of diallyl(fluoro)borane. Even with a triple excess of triallylborane, our attempts to move the equilibrium completely to monofluoro derivative **5** were not successful. Note that diallyl(chloro)borane can be easily generated *in situ* by a similar procedure.[6,7]

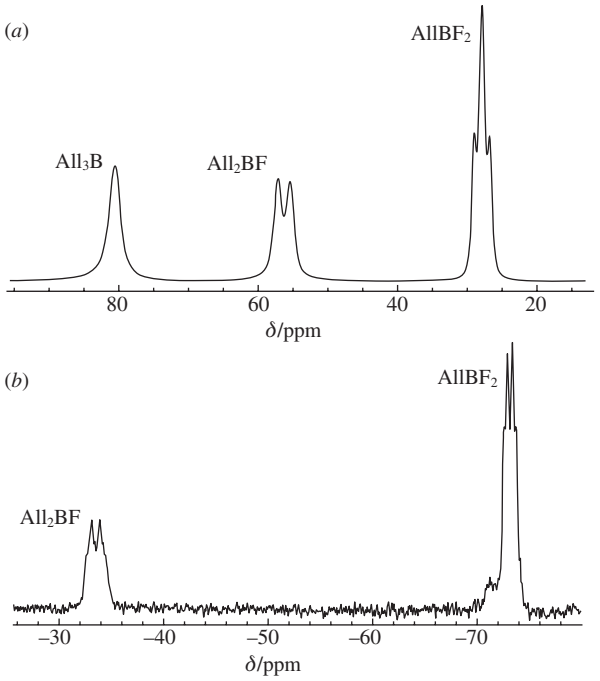
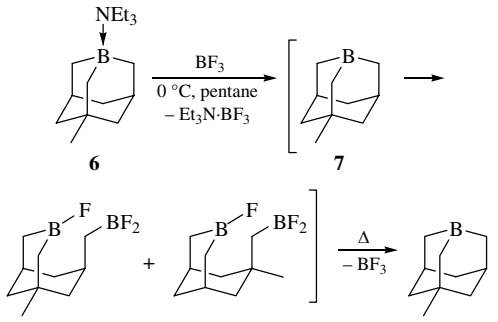


Figure 2 (*a*) ^{11}B and (*b*) ^{19}F NMR spectra of an equilibrated mixture of All_3B/BF_3 (2:1) (64.21 and 188.31 MHz, respectively; $CDCl_3$).

‡ **4** (as a mixture of *ca.* 5:1 *E*- and *Z*-isomers) in a 1:1 mixture with dipropylfluoroborane. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.77 [d, 2H, H(1) (**4b**), $^3J_{H(1)–H(2)}$ 6.6 Hz], 1.99 [br. s, 2H, H(1) (**4a**)], 5.01 [d, 1H, H(5)$_{cis}$ (**4a**), $^3J_{H(5)_{cis}–H(4)}$ 10.1 Hz], 5.12 [d, 1H, H(5)$_{trans}$ (**4a**), $^3J_{H(5)_{trans}–H(4)}$ 16.6 Hz], 5.11 [m, 2H, H(5) (**4b**)], 5.50 [dt, 1H, H(2) (**4b**), $^3J_{H(2)–H(3)}$ 10.0 Hz, $^3J_{H(2)–H(1)}$ 6.6 Hz], 5.72 [dt, 1H, H(2) (**4a**), $^3J_{H(2)–H(3)}$ 14.9 Hz, $^3J_{H(2)–H(1)}$ 7.6 Hz], 5.86 [dddd, 1H, H(3) (**4b**), $^3J_{H(3)–H(2)}$ 10.0 Hz, $^3J_{H(3)–H(4)}$ 9.7 Hz, $^4J_{H(3)–H(5)_{trans}}$ 6.2 Hz, $^4J_{H(3)–H(5)_{cis}}$ 6.2 Hz], 6.10 [dd, 1H, H(3) (**4a**), $^3J_{H(3)–H(2)}$ 14.9 Hz, $^3J_{H(3)–H(4)}$ 10.1 Hz], 6.32 [ddd, 1H, H(4) (**4a**), $^3J_{H(4)–H(5)_{trans}}$ 16.6 Hz, $^3J_{H(4)–H(5)_{cis}}$ 10.1 Hz, $^3J_{H(4)–H(3)}$ 10.1 Hz], 6.59 [ddd, 1H, H(4) (**4b**), $^3J_{H(4)–H(5)_{trans}}$ 15.9 Hz, $^3J_{H(4)–H(5)_{cis}}$ 9.7 Hz, $^3J_{H(4)–H(3)}$ 9.7 Hz]. ^{13}C-{^{1}H} NMR (50.32 MHz, $CDCl_3$) δ: 114.4 [C(5) (**4b**)], 115.4 [C(5) (**4a**)], 125.8 [C(2) (**4a**)], 131.0 [C(2) (**4b**)], 132.3 [C(3) (**4b**)], 133.6 [C(3) (**4a**)], 136.4 [C(4) (**4b**)], 136.7 [C(4) (**4a**)]. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ: 25.7 [t (**4a**), $^2J_{^{11}B–^{19}F}$ 77 Hz], 28.8 [t (**4b**), $^2J_{^{11}B–^{19}F}$ 86 Hz]. ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: –72.5 [q (**4a**), $^2J_{^{19}F–^{11}B}$ 77 Hz], –72.0 [q (**4b**), $^2J_{^{19}F–^{11}B}$ 86 Hz].

The ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra exhibited signals corresponding to both allyl(difluoro)borane **2** and diallyl(fluoro)borane **5**§ (Scheme 3, Figure 2).

One more example of a non-catalytic desymmetrization process represents the reaction of BF_3 with 1-boraadamantanes, unique highly strained cage triorganoboranes, possessing a set of unusual features of R_3B.[12] We have found that the treatment of 3-methyl-1-boraadamantane thriethylamine adduct **6** with BF_3 at 0 °C leads to 3-methyl-1-boraadamantane **7**, whose reaction with BF_3 gives rise to 3-fluoro-7-difluoroborylmethyl-3-borabicyclo[3.3.1]nonane derivatives **8** as a result of cage rupture (Scheme 4). The vacuum distillation of **8** gave back 3-methyl-1-boraadamantane molecule **7**¶ *via* a ring closure, similar to that usually applied to the synthesis of 1-boraadamantanes from 7-methylene-3-borabicyclo[3.3.1]nonane derivatives and boron hydrides.[12]



Scheme 4

In conclusion, the above results demonstrated three triorganoborane desymmetrization reactions proceeding in the absence of B–H catalysts usually required. The reaction of boron trifluoride with allylic boranes is obviously a general regularity and presents a convenient approach to allyldifluoroboranes, while the rupture of the 1-boraadamantane core with BF_3 is unexpected and represents a unique property of this cage compound.

This work was supported by the President of the Russian Federation (grant no. 2878.2006.3), the Russian Foundation for Basic Research (grant nos. 05-03-32953 and 05-03-33268) and the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (Programme no. 1).

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§ **5** in a mixture with **1** and **2** in *ca.* 1:1:2 ratio, prepared from 2 equiv. of triallylborane and 1 equiv. of BF_3. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ: 2.23 [br. s, 2H, H(1)], 4.99 [br. m, 2H, H(3)], 5.84 [ddt, 1H, H(2), $^3J_{H(2)–H(3)_{trans}}$ 17.6 Hz, $^3J_{H(2)–H(3)_{cis}}$ 9.5 Hz, $^3J_{H(2)–H(3)}$ 7.5 Hz]. ^{13}C-{^{1}H} NMR (50.32 MHz, $CDCl_3$) δ: 26–30 (very br., CB) 115.4 [C(3)], 134.6 [C(2)]. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ: 56.8 (d, $^1J_{^{11}B–^{19}F}$ 114 Hz). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: –33.8 (q, $^1J_{^{19}F–^{11}B}$ 114 Hz).

¶ The reaction mixture contains ~80% of **8** as well as **7** and BF_3·Et_3N. ^{11}B NMR (64.21 MHz, pentane) δ: –0.7 (s, BF_3·Et_3N), 28.0 [t, BF_2 (**8**), $^1J_{^{11}B–^{19}F}$ 79 Hz], 59.9 [d, BF (**8**), $^1J_{^{11}B–^{19}F}$ 98 Hz], 86.0 [s (**7**)]. ^{19}F NMR (188.31 MHz, pentane) δ: –148.5 (m, BF_3·Et_3N), –72.1 [q, 2F, BF_2 (**8**), $^1J_{^{19}F–^{11}B}$ 79 Hz], –39.0 [q, 1F, BF (**8**), $^1J_{^{19}F–^{11}B}$ 98 Hz].

7: 35% yield; bp 49–51 °C (2 Torr). Extremely sensitive to air. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.16 (s, 3H, Me), 1.2–1.7 (m, 12H, intricate multiplet of 1-boraadamantane core CH_2 protons), 2.90 [s, 2H, H(5), H(7)]. ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 33.8 (q, Me, 124.6), 37.6 [t, C(6), $^1J_{^{13}C–^1H}$ 130.2 Hz], 37–39 [br., C(9), C(10)], 44.4 [d, C(5), C(7), $^1J_{^{13}C–^1H}$ 137.6 Hz], 45.2 [t, C(4), C(8), $^1J_{^{13}C–^1H}$ 125.2 Hz], 45–47 [br., C(2)], 50.7 [s, C(3)]. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ: 82.6.

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Received: 24th April 2007; Com. 07/2919