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## Reactions of (Perfluoroalkyl)trimethoxyborates with Electrophilic Reagents

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**Abstract:** It is shown that interaction of (perfluoroalkyl)trimethoxyborates with the overall formula of  $K[R_F B(OMe)_3]$  ( $R_F = CF_3, C_2F_5$ ) with acyl chlorides, perfluoroacyl fluorides, etherate of  $BF_3$ , and sulfuric acid results in formation, as dependent on the nature of the electrophile, of (perfluoroalkyl)dimethoxyboranes, (perfluoroalkyl)trifluoroborates, (perfluoroalkyl)boroxines, and mixed anhydrides of perfluoroalkylboronic and sulfuric acids (boroxinesulfates).

**Keywords:** perfluoroalkylborates, perfluoroalkylboranes, trifluoroborates, boroxinesulfate, boroxines, boronic acids.

The ever growing interest towards perfluoroalkyl compounds of boron is due to the ever expanding sphere of their practical application, particularly, as fluoroalkylating agents, electrolytes, ionic liquids, weakly coordinating anions, and ligands [1].

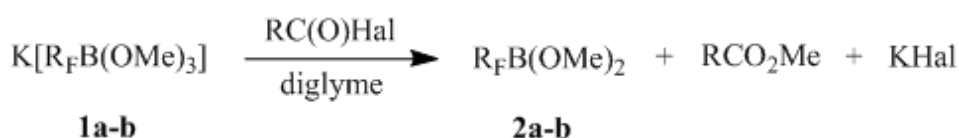
At the same time, despite the availability of such fluoroaliphatic derivatives of boron as alkali fluoroalkyltrimethoxyborates, the data on their reactivity are rather fragmentary. Thus, interaction with electrophilic reagents is represented only by demethoxylation under the action of silylating ( $ClSiMe_3$ ), sulfonylating ( $MeSO_2Cl$ ), and methylating ( $TsOMe$ ,  $TfOMe$ ) agents with formation of (fluoroalkyl)dimethoxyboranes as the only reaction products [1–2].

Reactions of borates with the overall formula of  $K[R_F B(OMe)_3]$  (**1a-b**) [ $R_F = CF_3$  (**1a**);  $R_F = C_2F_5$  (**1b**)] with electrophiles of different nature including Lewis and Brønsted acids were studied for further research of the chemical behavior of fluoroalkyltrialkoxymethylborates towards electrophilic reagents.

### Reactions of potassium (perfluoroalkyl)trimethoxyborates 1a-b with acyl halides

Salts **1a-b** undergo demethoxylation in a reaction with acetyl chloride, benzoyl chloride, or benzoyl bromide and form fluoroalkyldimethoxyboranes (cf. with the data of [2]). It should be noted that as opposed to  $AcCl$  and  $BzBr$ , easily reacting at  $\sim 25^\circ C$ , interaction between borates **1a-b** and  $BzCl$  requires heating up to  $55-60^\circ C$ .

#### Scheme 1

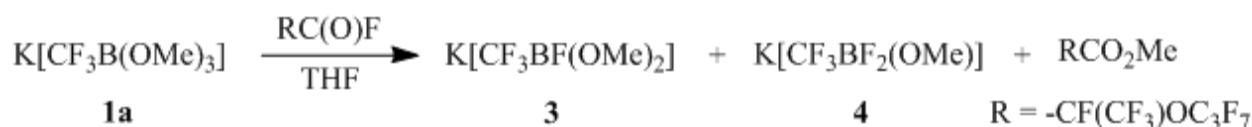


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Nos.	RF 1a-b	RC(O)Hal	Temp., oC	Time, h	Yield 2a-b, %
1	CF <sub>3</sub> ( <b>1a</b> )	AcCl	25	3	80 ( <b>2a</b> )
2	CF <sub>3</sub> ( <b>1a</b> )	BzBr	25	3	80 ( <b>2a</b> )
3	CF <sub>3</sub> ( <b>1a</b> )	BzCl	25	4	10 ( <b>2a</b> )
4	CF <sub>3</sub> ( <b>1a</b> )	BzCl	60	1.5	70 ( <b>2a</b> )
5	C <sub>2</sub> F <sub>5</sub> ( <b>1b</b> )	BzCl	60	1.5	70 ( <b>2b</b> )

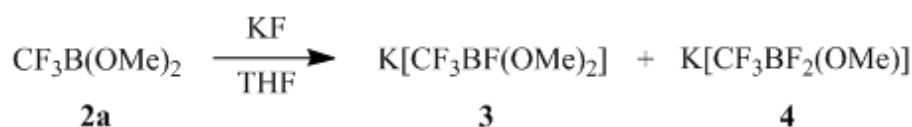
The composition of reaction products changes profoundly when perfluoroalkanoyl fluoride is used as the acylating agent. In this case, the reaction products are mono- and difluoroborates **3** and **4** at the ratio of 2 : 1 (according to the data of <sup>19</sup>F NMR).

#### Scheme 2



The ratio of salts **3** and **4** does not change when the reaction occurs in the temperature range of –75÷25 °C. Obviously, formation of fluoroborates **3** and **4** occurs as a result of interaction of the initially formed (trifluoromethyl)dimethoxyborane (**2a**) with KF, also being a reaction product, which is confirmed by countersynthesis of salts **3–4** from borane **2a** and KF.

#### Scheme 3



An increase in the amount of perfluoroacylfluoride introduced into the reaction results in the further substitution of methoxy groups by fluoride up to formation of (perfluoroalkyl)trifluoroborates **5a-b** as the only reaction products when three equivalents of perfluoroacyl fluoride are used.

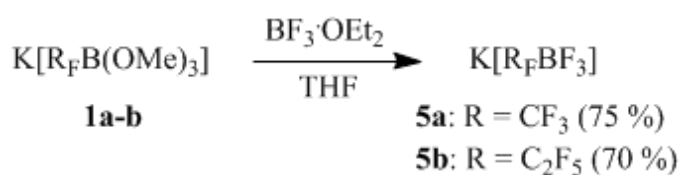
#### Scheme 4



### Reactions of potassium (perfluoroalkyl)trimethoxyborates **1a-b** with boron trifluoride etherate

We showed that the reaction of BF<sub>3</sub>•OEt<sub>2</sub> with borates **1a–b** is a convenient preparative method of trifluoroborates synthesis **5a-b**, though the yield of salts **5** in this case is somewhat lower as compared to the reaction in scheme 4.

#### Scheme 5



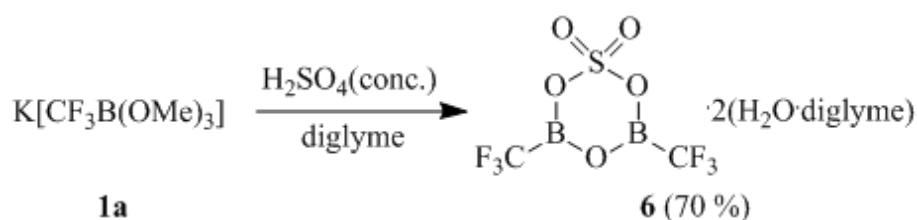
As opposed to the above method of synthesis of trifluoroborates **5a–b** in the reaction of hydrofluoric acid and salts **1a–b** [3–4], the suggested method is more convenient, as it allows carrying the reaction out in glass equipment. According to the data of [5], BF<sub>3</sub> was used to obtain sodium hydrotrifluoroborate, but application of BF<sub>3</sub> in synthesis of organotrifluoroborates has not been described earlier [6].

### Reactions of potassium (perfluoroalkyl)trimethoxyborates **1a-b** with sulfuric acid

It is known that the reaction between mineral acids (HCl, H<sub>2</sub>SO<sub>4</sub>, etc.) with borate salts containing various organic groups leads to formation of the corresponding boronic acids that interact with dehydrating reagents, e.g., concentrated sulfuric acid, and also in a number of cases, under drying or in the course of crystallization, forming the corresponding boroxines [7]. In particular, this method was used to obtain fluoroaromatic boronic acids and the corresponding boroxines [8–9]. However, perfluoroalkylboronic acids and their boroxines are not as yet described in the literature [1].

We found that interaction of potassium (trifluoromethyl)trimethoxyborate (**1a**) with concentrated sulfuric acid in a diglyme solution in a high yield results in formation of (trifluoromethyl)boroxinesulfate **6** isolated from the reaction mixture in the form of a solvate containing two molecules of water and two molecules of diglyme.

#### Scheme 6



Formation of boroxinesulfates in such reactions has not been registered earlier. The structure of solvate complex **6** is confirmed by the data of elemental analysis and X-ray diffraction study (Fig. 1).

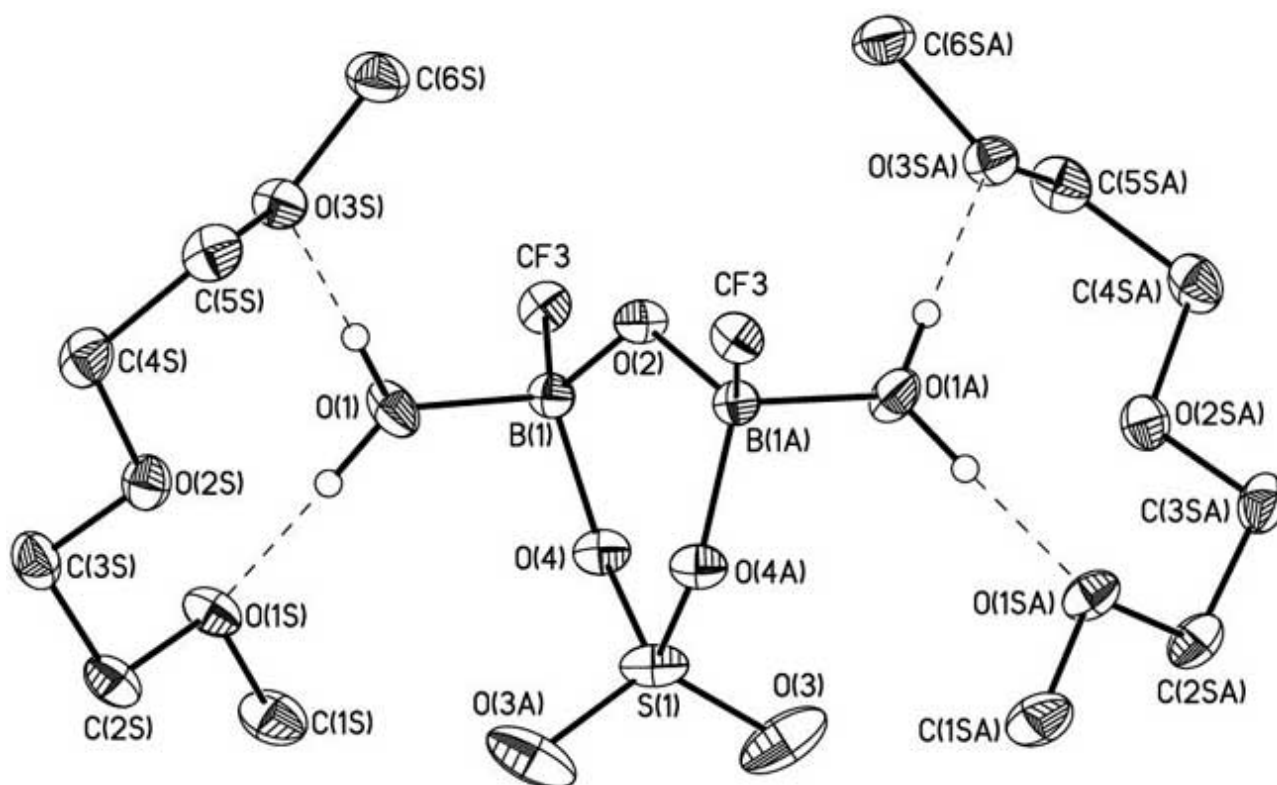


Fig. 1. The general view of **6** in representation of non-hydrogen atoms by probability ellipsoids of thermal vibrations. Hydrogen atoms of diglyme molecules are omitted for clarity.

At the same time, potassium (pentafluoroethyl)trimethoxyborate (**1b**) forms under similar conditions (pentafluoroethyl)boroxine **7b** isolated in the form of a solvate that also contains two molecules of water and two molecules of diglyme according to the data of X-ray diffraction study (Fig. 2) and elemental analysis.

### Scheme 7

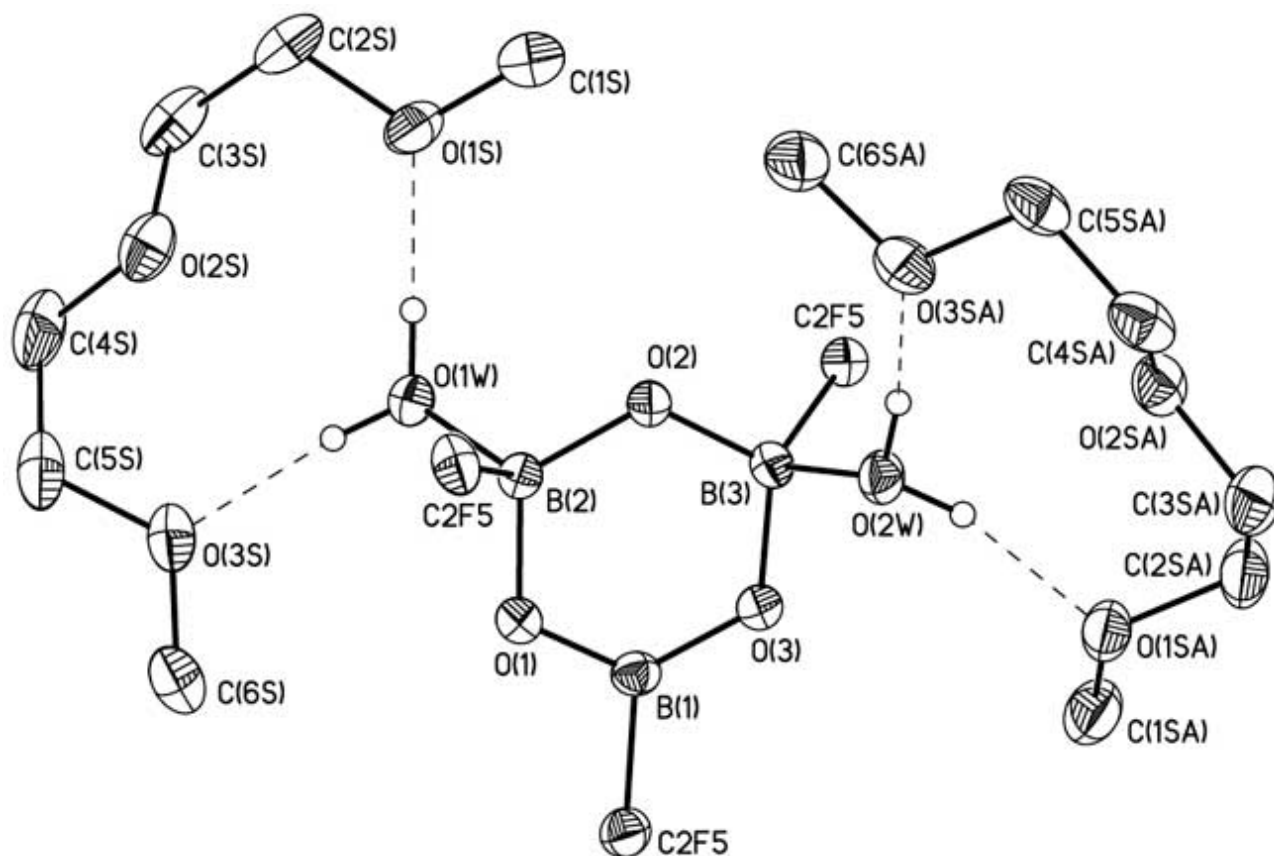
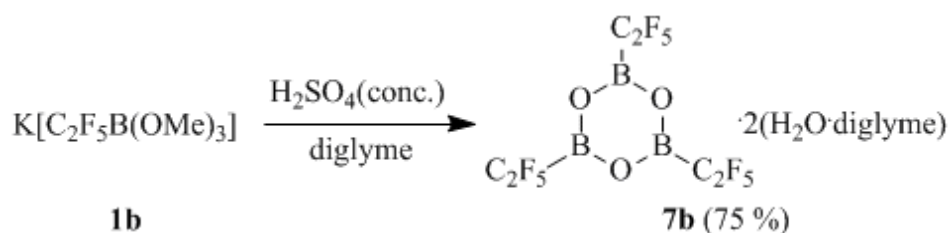
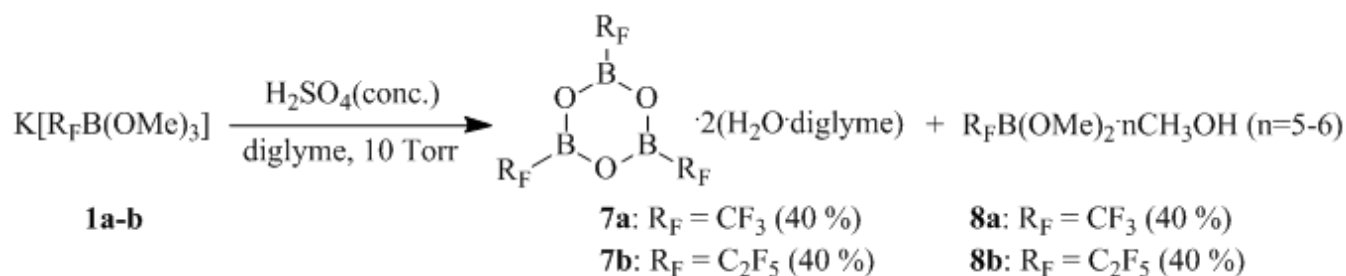


Fig. 2. The general view of **7b** in representation of non-hydrogen atoms by probability ellipsoids of thermal vibrations. Hydrogen atoms of diglyme molecules are omitted for clarity.

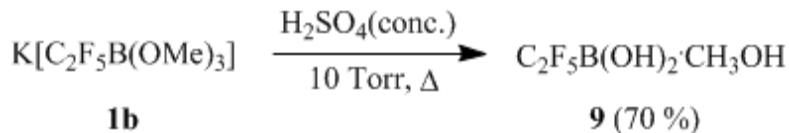
The composition of the products of a reaction between **1a–b** and sulfuric acid changes in the case of a reaction under reduced pressure (10 torr). In this case, irrespective of borate salt **1a–b** used in the reaction, (perfluoroalkyl)boroxines **7a–b** and (perfluoroalkyl)boranes **8a–b** are formed.

### Scheme 8



One should point out that the reaction between sulfuric acid and salt **1b** under reduced pressure (10 torr) in the absence of a solvent leads to formation of pentafluoroethylboronic acid distilled from the reaction mixture in the form of a methanol adduct **9**.

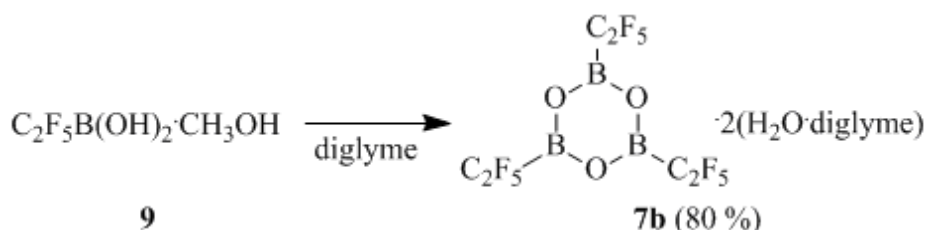
### Scheme 9



Compound **9** represents a colorless sirupy liquid and can be considered as an ansolvate acid  $\text{H}[\text{C}_2\text{F}_5\text{B}(\text{OH})_2(\text{OMe})]$  [10].

It is of interest that dissolution of compound **9** in diglyme in the absence of any dehydrating reagents results in practically immediate formation of (pentafluoroethyl)boroxine **7b** that is precipitates in the form of crystals.

#### Scheme 10

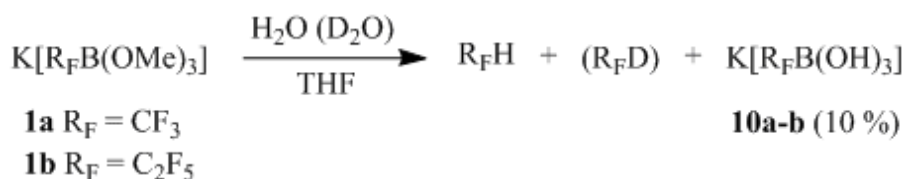


A similar reaction of borate **1a** resulted in formation of a negligible amount of a compound with an unclear structure containing, according to the data of  $^{19}\text{F}$  NMR, a  $\text{CF}_3\text{BF}_2$  fragment, which in our opinion, is an indirect proof of degradation of the trifluoromethyl group.

### Reactions of potassium (perfluoroalkyl)trimethoxyborates **1a-b** with water

(Perfluoroalkyl)trimethoxyborate salts **1a-b** in water undergo deboronation with formation of the corresponding hydroperfluoroalkanes, which was earlier observed by other researchers [11]. Therefore, their spectral data obtained in a  $\text{D}_2\text{O}$  solution [2, 12] are most probably erroneous and characterize the hydrolysis product. Thus, we showed that the main products of an addition reaction between water or deuterated water and potassium (perfluoroalkyl)trimethoxyborates **1a-b** in a THF solution are hydroperfluoroalkanes (or deuteroperfluoroalkanes); the relative content of perfluoroalkylborates **10a-b** (characterized using  $^{19}\text{F}$  NMR) does not exceed 10 %.

#### Scheme 11



At the same time, one should point out that no deboronation is observed for a prolonged time (for about a month) when (trifluoromethyl)boroxinesulfate **6**, (perfluoroalkyl)boroxines **7a-b**, and ansolvate acid **9** are dissolved in water or an aqueous–ether mixture. Aqueous solutions of these compounds are characterized by high acidity and are titrated by aqueous alkali solutions.

Compound	pH of aqueous solution
<b>6</b>	2.8
<b>7a</b>	2.5
<b>7b</b>	3.2
<b>9</b>	2.7

Thus, we showed that the fluoroalkyl group remains at the boron atom in the interaction of borates **1a-b** with acyl chlorides, perfluoroacyl fluorides, etherate of  $\text{BF}_3$ , and sulfuric acid and

(perfluoroalkyl)dimethoxyboranes, (perfluoroalkyl)trifluoroborates, (perfluoroalkyl)boroxines, and mixed anhydrides of perfluoroalkylboronic and sulfuric acids (boroxinesulfates) are formed, as dependent on the nature of the electrophile.

## Experimental

$^{19}\text{F}$ , and  $^{11}\text{B}$  NMR spectra were recorded using a Bruker AVANCE-300 and 400 spectrometer at 282, and 128 MHz, accordingly, in  $\text{D}_2\text{O}$  or with  $\text{D}_2\text{O}$  as an external standard. Chemical shifts in  $^{19}\text{F}$  spectra are given in ppm vs.  $\text{CFCl}_3$ . Chemical shifts in  $^{11}\text{B}$  spectra are given in ppm vs.  $\text{BF}_3\cdot\text{OEt}_2$ .

Potassium (perfluoroalkyl)trimethoxyborates **1a-b** were obtained earlier according to the earlier described method using THF or diglyme as a solvent [2, 4]. 93-95 % sulfuric acid was used in reactions.

### Synthesis of (perfluoroalkyl)dimethoxyboranes 2a-b.

Benzoyl chloride (7.0 g, 50 mmol) was added dropwise to a solution of salt **1a** or **1b** (50 mmol) in absolute diglyme (50 ml) under mixing at the temperature of 55-60°C under vacuum (10 torr) and the volatile reaction product was distilled into a receiver (-78°C). After all benzoyl chloride was added, the reaction mixture was mixed for 1.5 h at 55-60°C and then the pressure was adjusted to the atmospheric pressure by adding an inert gas.

**(Trifluoromethyl)dimethoxyborane (2a).** Yield, 70 %.

**(Pentafluoroethyl)dimethoxyborane (2b).** Yield, 70 %.

### Synthesis of potassium (perfluoroalkyl)trifluoroborates 5a-b.

**A:** Perfluoro-2-propoxypropionyl fluoride (49.8 g, 150 mmol) was added to a solution of salt **1a** or **1b** (50 mmol) in absolute THF (50 ml) under cooling by cold water. The reaction mixture was mixed for 3 h at 50°C and evaporated to dryness under vacuum (10 torr). The obtained solid deposition was recrystallized.

**Potassium (trifluoromethyl)trifluoroborate (5a).** Recrystallized from isopropanol. Yield, 95 %.

**Potassium (pentafluoroethyl)trifluoroborate (5b).** Recrystallized from a heptane–isopropanol mixture. Yield, 93 %.

**B:**  $\text{BF}_3\cdot\text{OEt}_2$  (7.1 g, 50 mmol) was added dropwise to a solution of salt **1a** or **1b** (50 mmol) in absolute THF (50 ml) under mixing at the temperature of -30°C. The reaction mixture was heated to the room temperature ~25°C for 30 min and mixed at the room temperature for 3 h, evaporated under vacuum (10 torr) and the residue was recrystallized. The yield of **5a**, 75 %; that of **5b**, 70 %.

### Interaction of salts 1a-b with $\text{H}_2\text{SO}_4$ in a diglyme solution.

$\text{H}_2\text{SO}_4$  (5.3 g, 50 mmol) was added dropwise to a solution of salt **1a** or **1b** (50 mmol) in absolute diglyme (50 ml) under mixing at the temperature of -50°C. The reaction mixture was heated to the room temperature ~25°C and mixed for 30 min. Water (5 ml) was added and the whole was mixed for another 30 min. The deposit was filtered, the solvent was evaporated under vacuum (0.5 torr) at the temperature not above 25-30°C, the residue was dissolved in chloroform (50 ml). The obtained solution was filtered, evaporated in air (in a glass). The crystals formed were filtered and dried under vacuum (0.5 torr).

**A complex of (trifluoromethyl)boroxinesulfate with diglyme and water (6).** Yield, 70 %.  $^{19}\text{F}$  NMR  $\delta$ : -76.5 (br. s.,  $\text{CF}_3$ );  $^{11}\text{B}$  NMR  $\delta$ : -0.7 (br. s). Found (%): C, 29.00; H, 5.58; B, 3.75; F, 19.79; S, 5.57.  $\text{C}_{14}\text{H}_{32}\text{B}_2\text{F}_6\text{O}_{13}\text{S}$ . Calculated (%): C, 29.19; H, 5.60; B, 3.75; F, 19.79; S, 5.57.

**A complex of (pentafluoroethyl)boroxine with diglyme and water (7b).** Yield, 75 %.  $^{19}\text{F}$  NMR  $\delta$ : -83.4 (s, 3F,  $\text{CF}_3$ ), -135.4 (s, 2F,  $\text{CF}_2$ );  $^{11}\text{B}$  NMR  $\delta$ : 3.3 (br. s). Found (%): C, 29.19; H, 4.50; B, 4.37; F, 38.37.  $\text{C}_{18}\text{H}_{32}\text{B}_3\text{F}_{15}\text{O}_{11}$ . Calculated (%): C, 29.14; H, 4.35; B, 4.37; F, 38.41.

### Interaction of salts 1a-b with $\text{H}_2\text{SO}_4$ in a diglyme solution under vacuum.

$\text{H}_2\text{SO}_4$  (5.3 g, 50 mmol) was added dropwise to a solution of salt **1a** or **1b** (50 mmol) in absolute diglyme (50 ml) under mixing at the temperature of ~25°C under vacuum (10 torr) and the volatile reaction products were distilled into a receiver (-78°C). After all  $\text{H}_2\text{SO}_4$  was added, the reaction mixture

was mixed for 30 min and then the pressure was adjusted to the atmospheric pressure by adding an inert gas.

Water (5 ml) was added to the reaction mixture, the whole was mixed for 30 min, the deposit was filtered, the solvent was evaporated under vacuum (0.5 torr) at the temperature not above 25–30°C and the residue was dissolved in chloroform (50 ml). The obtained solution was filtered and left to evaporate slowly in air (in a glass). The crystals formed were filtered and dried under vacuum (0.5 torr).

The distillate obtained in the experiment was distilled,  $T_{\text{boil}} = 55\text{--}70^\circ\text{C}$ . Diglyme remained in the still liquor (about 15 wt. %).

**A complex of (trifluoromethyl)boroxine with diglyme and water (7a).** Yield, 40 %.  $^{19}\text{F}$  NMR  $\delta$ : -76.8 (br. s.,  $\text{CF}_3$ );  $^{11}\text{B}$  NMR  $\delta$ : -0.3 (br. s). Found (%): C, 30.32; H, 5.45; B, 5.57; F, 28.78.  $\text{C}_{15}\text{H}_{32}\text{B}_3\text{F}_9\text{O}_{11}$ . Calculated (%): C, 30.44; H, 5.45; B, 5.48; F, 28.89.

#### Interaction between salt **1b** and $\text{H}_2\text{SO}_4$ under vacuum.

$\text{H}_2\text{SO}_4$  (40 g, 376 mmol) was added dropwise to dry salt **1b** (13.1 g, 50 mmol) under mixing and cooling to the temperature of 5–10°C under vacuum (10 torr) taking care that the salt is not pulverized. Further, the mixture is heated to the temperature of 100–150°C, in the course of which a colorless viscous liquid distilled in the range of 60–80°C is distilled.

**Pentafluoroethylboronic acid, a complex with methanol (9).** Yield, 70 %.  $^{19}\text{F}$  NMR  $\delta$ : -84.9 (s, 3F,  $\text{CF}_3$ ), -136.3 (s, 2F,  $\text{CF}_2$ ). Found (%): C, 18.93; H, 3.24; B, 5.32; F, 48.38.  $\text{C}_3\text{H}_6\text{BF}_5\text{O}_3$ . Calculated (%): C, 18.39; H, 3.09; B, 5.52; F, 48.49.

*Crystallographic data: CCDC 889080 and 889081 contain the supplementary crystallographic data for 6 and 7b. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge, CB21EZ, UK; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).*

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