Polyfluoroorganoboron-Oxygen Compounds. 2 [1] Base-catalysed Hydrodeboration of Polyfluorophenyl(dihydroxy)boranes

H.-J. Frohn^{a,*}, N. Y. Adonin^b, V. V. Bardin^b, and V. F. Starichenko^b

^a Duisburg, Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität

^b Novosibirsk/Russia, N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Sibirian Branch of Russian Academy of Sciences

Received February 11th, 2002; revised May 30th, 2002.

Dedicated to Professor Rüdiger Mews on the Occasion of his 60th Birthday

Abstract. Polyfluorinated phenyl(dihydroxy)boranes $C_6H_{5-n}F_nB$ -(OH)₂ (n = 3 - 5) underwent hydrodeboration (formal replacement of the (dihydroxy)boryl group by hydrogen) in the presence of bases (MeOH, 33 % H₂O-MeOH, KOH (1 equiv.)/33 % H₂O-MeOH, pyridine and 9 % D₂O-pyridine) and formed the fluoroaromatic compounds ArH or ArD, respectively. The rate of

reaction depends on the number of fluorine atoms in the phenyl group and on the position of the fluorine atoms, relative to the $B(OH)_2$ substituent.

Keywords: Polyfluorophenyl(dihydroxy)boranes (Polyfluorophenylboronic acids); Hydrodeboration; NMR spectroscopy

Polyfluororganische Bor-Sauerstoff Verbindungen. 2 [1]

Die Hydrodeborierung von Polyfluorphenyl(dihydroxy)boranen unter basischen Bedingungen.

Inhaltsübersicht. Polyfluorierte Phenyl(dihydroxy)borane $C_6H_{5-n}F_nB$ -(OH)₂ (n = 3 - 5) unterliegen in Gegenwart von Basen (MeOH, 33 % H₂O-MeOH, KOH (1 Äquiv.)/33 % H₂O-MeOH, Pyridin und 9 % D₂O-Pyridin) einer Hydrodeborierungsreaktion (formaler Ersatz der (Dihydroxy)borylgruppe durch Wasserstoff) und bil-

Introduction

Recently, we have reported a general preparative procedure for polyfluorinated aryl(dihydroxy)boranes $C_6H_{5-n}F_nB-(OH)_2$ and tri(aryl)boroxins ($C_6H_{5-n}F_nBO)_3$ (n = 3 - 5) [1]. The latter were obtained by thermal dehydration of the corresponding aryl(dihydroxy)boranes (often named arylboronic acids) ArB(OH)₂ at 100 °C or by treatment of the acids with SOCl₂ in ether at 20 °C. Despite the fact that some of these compounds [2,4-, 2,5-, 2,6-, 3,4-, 3,5- $C_6H_3F_2B(OH)_2$, and $C_6F_5B(OH)_2$] are now commercially available [2], their basic reactivity has not been investigated. *Chambers* and *Chivers* have found that pentafluorophenyl-(dihydroxy)borane underwent a slow hydrodeboration in aqueous solution (20 % conversion at 20 °C within 2 days)

* Prof. Dr. H.-J. Frohn

Fachgebiet Anorganische Chemie

Gerhard-Mercator-Universität Duisburg Lotharstr. 1 D-47048 Duisburg Fax: (+49) 2 03-3 79 22 31

e-mail: frohn@uni-duisburg.de

den die entsprechenden Fluoraromaten ArH oder ArD. Die Reaktionsgeschwindigkeit hängt dabei von der Anzahl der Fluoratome in der Arylgruppe und der relativen Stellung der Fluoratome zum $B(OH)_2$ -Substituenten ab.

and decomposed quickly in aqueous ethanol (45 min. at 20 °C). $C_6F_5B(OH)_2$ was more stable in aqueous acetone (several hours at 20 °C) and no decomposition was found in an acidic solution with 2 N HCl/ethanol (20 °C, 1 h). The oxidation of $C_6F_5B(OH)_2$ with 85 % H_2O_2 at 20 to 50 °C gave pentafluorophenol in 91 % yield [3]. Fluorine-containing aryl(dihydroxy)boranes formed the corresponding potassium aryltrifluoroborates after treatment with K [HF₂] in aqueous methanol [4, 5]. To our knowledge, no information exists about the reactivity of tri- and tetrafluorophenyl(dihydroxy)boranes.

The substitution of boron in the C-B bond by hydrogen, either under acid- or base-catalysis (electrophilic and nucleophilic hydrodeboration), is one of the fundamental properties of aryl(dihydroxy)boranes [6, 7]. In 1930 *Ainley* and *Challenger* reported that phenyl(dihydroxy)borane was unreactive in 5 % boiling aqueous NaOH (20 h) but formed benzene slowly when heated with a concentrated aqueous solution of NaOH or with water under pressure (140 – 150 °C, 40 h) [8]. *Kuivila et al.* have studied the kinetics of the base-catalysed hydrodeboration of several aryl(dihydroxy)boranes ArB(OH)₂ [Ar = C₆H₅, 2-, 3- and 4-C₆H₄X (X = F, Cl, CH₃, OCH₃)] (90 °C, preferentially at pH 6.70) [9]. In the present work we investigate the hydrodeboration of pentafluorophenyl- (1), 2,3,4,5-tetrafluorophenyl- (2), 2,3,4,6-tetrafluorophenyl- (3), 2,3,5,6-tetrafluorophenyl-(4), 2,4,6-trifluorophenyl- (5), 3,4,5-trifluorophenyl- (6), 2,4-difluorophenyl- (7) and 2,6-difluorophenyl- (8) (dihydroxy)boranes in the presence of bases (MeOH, 33 % H₂O-MeOH, KOH (1 equiv.)/33 % H₂O-MeOH, pyridine and 9 % D₂O-pyridine).

Results and Discussion

The aryl(dihydroxy)boranes 1 - 8 dissolve in aprotic polar solvents (acetonitrile, acetone) and form stable solutions. The comparison of the ¹⁹F NMR spectra of solutions of 1 in MeCN (basic solvent) and in CH₂Cl₂ (neutral, "noncoordinating" solvent) suggested a donor-acceptor molecular interaction of 1 with a base [1]. However, the dissolution of 1 in methanol (protic polar solvent) at 20 - 30 °C caused the appearance of pentafluorobenzene (9a) (ca. 5%conversion within 15 minutes). The rate of hydrodeboration was substantially increased in 33 % H₂O-MeOH or after addition of water to a solution of 1 in CH₂Cl₂. For instance, the hydrodeboration of 1 in 33 % H₂O-MeOH was 81 %after 20 minutes and completed after 2 h hours. The addition of KOH (1 equivalent) shortened the time of complete hydrodeboration of 1 in aqueous methanol to 10 - 15minutes. The reaction of 1 with anhydrous pyridine proceeded exothermally and resulted in the immediate formation of pentafluorobenzene (9a).

$$C_6F_5B(OH)_2 \xrightarrow{Base} C_6F_5H$$

Base = MeOH, aqueous MeOH, H_2O in CH_2Cl_2 , KOH in aqueous MeOH

The solutions of tetrafluorophenyl(dihydroxy)boranes (2 - 4) in MeOH were more stable than that of 1 and showed no notable decomposition within 1 h. The hydrodeboration of 2,3,4,6-tetrafluorophenyl(dihydroxy)borane (3) in anhydrous pyridine also proceeded more slowly with respect to 1. After 20 min. the molar ratio of borane 3 to 1,2,3,5-tetrafluorobenzene (10) was 4 : 1 (¹⁹F NMR).

$$5-XC_6F_4B(OH)_2 \xrightarrow{P_y} 5-XC_6F_4H$$
$$X = F (1) \text{ (few min.), H (3) } (2 - 3 \text{ hours)}$$

We undertook a detailed investigation of the hydrodeboration of polyfluoroaryl(dihydroxy)boranes (1 - 8) using 9 % D₂O in pyridine. The essential results were (a) the clear dependence of the reaction rate on the number of fluorine atoms on the aryl group and on the position of the fluorine atoms, relative to the B(OH)₂ substituent and (b) the regiospecific substitution of the boron-containing substituent by deuterium (quantitative yield) in all cases. Pentafluorophenyl(dihydroxy)borane was the most reactive acid in this group and yielded deuteropentafluorobenzene (9b). The marked differences in reactivity within the series of isomers of $C_6H_3F_2B(OH)_2$ (7, 8), $C_6H_2F_3B(OH)_2$ (5, 6) and $C_6HF_4B(OH)_2$ (2, 3, 4) are reflected in the data presented in Table 1.

$$C_6H_{5-n}F_nB(OH)_2 \xrightarrow{D_2O-Py} C_6H_{5-n}F_nD$$

Table 1Total conversion of aryldihydroxyboranes $ArB(OH)_2$ into
deuteropolyfluorobenzenes ArD in 9 % D_2O -pyridine (v/v)

Aryl group		Temperature, °C	Time of conversion, min.
C_6F_5	1	25	< 3 - 5
2,3,4,5-C ₆ HF ₄	2	100	50
2,3,4,6-C ₆ HF ₄	3	32	210 ^{a)}
2,3,4,6-C ₆ HF ₄	3	100	15
2,3,5,6-C ₆ HF ₄	4	32	60
2,4,6-C ₆ H ₂ F ₃	5	100	90
3,4,5-C ₆ H ₂ F ₃	6	100	180, no reaction
$2,4-C_6H_3F_2$	7	100	19 hours ^{b)}
$2,6-C_6H_3F_2$	8	100	150

a) Conversion 82 %.

^{b)} Conversion 53 %.

Based on the product analysis by ¹⁹F NMR spectroscopy we estimated the rates of disappearance of $ArB(OH)_2$ (2 – 5, 7 and 8) in 9 % D₂O-pyridine at 32 °C and 100 °C (Figures 1 and 2) and calculated k (the observed rate constant). Compounds 1 and 6 were not examined because of the reactivity of the former being to high whereas the latter was too unreactive. The pseudo-first-order values of k were calculated taking into account an excess of the base.

In the series of the three isomeric acids $C_6HF_4B(OH)_2$ the influence of the position of the hydrogen atom relative to the B(OH)₂ group becomes obvious (Figure 1).There is a significant decrease in the hydrodeboration reaction from *p*-H [4, $k(32 \ ^{\circ}C) = (6.0 \pm 0.6) \times 10^{-2} \text{ min.}^{-1}$] over *m*-H [3, $k(32 \ ^{\circ}C) = (0.83 \pm 0.1) \times 10^{-2} \text{ min.}^{-1}$] to *o*-H [2, $k(32 \ ^{\circ}C) = 0.009 \times 10^{-2} \text{ min.}^{-1}$, calculated from the experimental results at 100 \ ^{\circ}C]. The higher importance of the position of fluorine atoms over the number of fluorine atoms is best demonstrated by the comparison of 2,4,6- $C_6H_2F_3B(OH)_2$ [5, $k(100 \ ^{\circ}C) = (6.8 \pm 0.2) \times 10^{-2} \text{ min.}^{-1}$] and 2,3,4,5- $C_6HF_4B(OH)_2$ [2, $k(100 \ ^{\circ}C) = (4.2 \pm 0.1) \times 10^{-2} \text{ min.}^{-1}$] (Figure 2). The presence of only one fluorine atom in the *o*-position in **2** is responsible for this result.

Principally, it seems reasonable that the hydrodeboration of fluorinated aryl(dihydroxy)boranes proceeds under basecatalysis via an intermediate species involving four-coordinate boron. Based on his kinetic measurements, *Kuivila et al.* proposed a two-step mechanism of hydrodeboration for monosubstituted aryl(dihydroxy)boranes $\text{RC}_6\text{H}_4\text{B}(\text{OH})_2$ in water (90 °C, pH 6.0 - 6.7) [9]. (Scheme 1).





Figure 1 Deuterodeboration of penta- and tetrafluorophenyl(dihydroxy)boranes (1-4) in 10 % D₂O - pyridine at 32 °C



Figure 2 Deuterodeboration of fluoro-containing phenyl(dihydroxy)boranes 2. 5, 7 and 8 in D_2O -pyridine at 100 °C



 $[RC_6H_4B(OH)_3]^- + H_2O \longrightarrow RC_6H_4H + [HO]^- + B(OH)_3$

Although no direct evidence for the formation of the aryl(trihydroxy)borate anion was presented, this assumption is reasonable, even for relatively weak Lewis acids. Furthermore, the ¹⁹F NMR spectra of the para-fluorinated aryl(dihydroxy)boranes 4-FC₆H₄B(OH)₂ and 3-Cl-4-FC₆H₃B(OH)₂ showed a significant low-frequency shift of the fluorine resonance in aqueous alkaline solution with respect to that in aqueous solution which illustrated the change of the B(OH)₂ group into a strongly electron-donating substituent [10]. However, the replacement of several hydrogen atoms in the phenyl group by fluorine atoms increases both the Lewis, as well as the Brønsted acidity of aryl(dihydroxy)boranes. This circumstance allows, in addition to the acid-base adduct formation, to propose the deprotonation of polyfluorophenyl(dihydroxy)boranes by a strong base (OH⁻, pyridine) and the generation of aryl(hydroxy)oxyborate anions [ArB(OH)O]⁻ with a three-coordinated boron atom or the strong polarization of the B-O-H bond by a hydrogen-bridge interaction with the base: $B\!-\!O^{\delta-}\!\cdots\!H^{\delta+}\!\cdots\!Base$. For example, the hydrodeboration of 1 with the sterically hindered 2,6-di(tert-butyl)pyridine (neat, in excess or in toluene solution) should proceed more likely via deprotonation of 1 than via the formation of the adduct $C_6F_5B(OH)_2$ · Base. Also, the heterogeneous reaction of 1 with anhydrous K_2CO_3 in toluene can include a deprotonation step.

$$C_6F_5B(OH)_2 \xrightarrow{Base, 20 \circ C} C_6F_5H$$

Base = $2,6-(tert-Bu)_2C_5H_3N$ (neat or in toluene solution, 3 - 5 min.); K₂CO₃ in toluene (24 h)

In general, the intermediate formation of the anions $[ArB(OH)_3]^-$ or $[ArB(OH)O]^-$ is expected to influence the ¹⁹F NMR spectroscopic characteristics of the fluorinated aryl group Ar. The position of the resonances of the polyfluorinated aryl(trihydroxy)borate salts should not be significantly distinguished from those of the known polyfluoroaryl(trifluoro)borates [5] or -(trialkoxy)borates [11]. However, we did not observe any remarkable difference in the ¹⁹F NMR spectra of fluorinated phenyl(dihydroxy)boranes in different basic solvents, either in acetonitrile, acetone or ether [1], or in protic media (MeOH, 33 % H₂O-MeOH or in 9 % D_2O -pyridine) or in anhydrous pyridine (Table 2). This spectroscopic result can be caused by a low equilibrium concentration of the $[ArB(OH)_3]^-$ anion (Scheme 1) or of the acid-base adduct $ArB(OH)_2$ · base or by a fast reaction of the deprotonated form of the acid $[ArB(OH)O]^{-}$ or its polarized form (Scheme 2).

Arvl group		Solvent	Chemical shifts, ppm				
5.6.4			F-2	F-3	F-4	F-5	F-6
$C_6F_5^{a)}$	1	Acetone-d ₆	-132.61	-163.50	-154.72	-163.50	-132.61
$C_{6}F_{5}$	1	MeOH	-132.44	-162.75	-154.11	-162.75	-132.44
C_6F_5	1	33 % H ₂ O-MeOH	-132.14	-162.30	-153.69	-162.30	-132.14
2,3,4,5-C ₆ HF ₄ ^{a)}	2	Acetone-d ₆	-131.69	-158.17	-155.27	-141.14	
2,3,4,5-C ₆ HF ₄	2	9 % D ₂ O−Py	-130.66	-156.80	-154.64	-139.50	
2,3,4,5-C ₆ HF ₄	2	MeOH	-131.71	-157.60	-155.43	-140.14	
$2,3,4,6-C_6HF_4^{a}$	3	CD ₃ CN	-125.56	-167.16	-131.51		-105.80
2,3,4,6-C ₆ HF ₄	3	9 % D ₂ O-Py	-125.32	-166.79	-132.41		-105.20
2,3,4,6-C ₆ HF ₄	3	МеОН	-126.13	-167.44	-131.61		-106.20
2,3,4,6-C ₆ HF ₄	3	Ру	-124.59	-166.31	-131.98		-104.65
2,3,5,6-C ₆ HF ₄ ^{a)}	4	Acetone-d ₆	-133.70	-140.34		-140.34	-133.70
2,3,5,6-C ₆ HF ₄	4	9 % D ₂ O-Py	-133.48	-140.30		-140.30	-133.48
2,3,5,6-C ₆ HF ₄	4	МеОН	-133.59	-139.30		-139.30	-133.59
$2,4,6-C_6H_2F_3^{(a)}$	5	Acetone-d ₆	-99.95		-107.67		-99.95
$2,4,6-C_6H_2F_3$	5	9 % D ₂ O-Py	-100.79		-109.01		-100.79
3,4,5-C ₆ H ₂ F ₃ ^{a)}	6	Acetone-d ₆		-136.41	-159.65	-136.41	
3,4,5-C ₆ H ₂ F ₃	6	$9\% D_2O-P_V$		-139.08	-162.46	-139.08	

-103.16

-103.65

-101.37

-101.64

Table 2 ¹⁹ F NMR spectroscopic data of fluorinated phenyl(dihydroxy))boranes ArB	$(OH)_2$
---	--------------	----------

Acetone-d₆

Acetone-d₆

9% D₂O-Py

9% D₂O-Py

a) Reference [1].

2,6-C₆H₃F₂^{a)}

2,4-C₆H₃F₂^{a)}

 $2,6-C_6H_3F_2$

2,4-C₆H₃F₂

Scheme 2

first step:		
ArB(OH) ₂ + base		[ArB(OH)O]⁻ + [Base-H]⁺
or		
ArB(OH) ₂ + base		ArB(OH)O ^{ŏ–} …H ^{ŏ+} …Base

7

7

8

8

second step:

 $[ArB(OH)O]^-$ or $ArB(OH)O^{\delta-} \longrightarrow ArH$

alternatively

 $[ArB(OH)O]^-$ or $ArB(OH)O^{\delta-} \longrightarrow \langle Ar^- \rangle$

 $\langle Ar^{-} \rangle + H-A \rightarrow ArH + A^{-} (H-A = H_2O, [Base-H]^+, HO-B \langle \rangle$

Our present experimental data do not allow us to decide between the aryl(trihydroxy)borate and aryl(hydroxy)oxyborate anion or the hydrogen-bridged species as the reactive key intermediate and precursor to ArH. Further investigations in this field are in progress.

Experimental

The NMR spectra were recorded on the BRUKER spectrometer WP 80 SY (19F at 75.39 MHz) at 32 °C. The chemical shifts are referenced to CCl₃F (¹⁹F) (with C₆F₆ as secondary reference, $\delta =$ -162.9 ppm). The yields of the reaction products were determined by ¹⁹F NMR spectroscopy using the internal quantitative reference C₆H₅CF₃.

Pyridine, 2,6-di(tert-butyl)pyridine, methanol and toluene were purified by standard procedures. Toluene was stored over molecular sieve (4 Å) before use.

Hydrodeboration of 1 in aqueous methanol

Aryl(dihydroxy)borane 1 (30 mg, 0.14 mmol) was dissolved in methanol (0.20 ml) and water (0.10 ml) at 20 °C and the progress of the reaction was monitored by ¹⁹F NMR spectroscopy over several hours until the hydrodeboration was completed.

-103.16

-103.65

Hydrodeboration of 1 with KOH in aqueous methanol

-107.65

-109.19

A 2 M solution of KOH in methanol (0.12 mmol KOH, 0.062 ml CH₃OH) was added to the mixture of methanol (0.139 ml) and water (0.100 ml) before aryl(dihydroxy)borane 1 (26 mg, 0.12 mmol) was dissolved. The solution was periodically examined by ¹⁹F NMR spectroscopy during several hours.

Hydrodeboration of aryl(dihydroxy)boranes (arylboronic acids) with pyridine or 2,6-di(tert-butyl)pyridine

A. Aryl(dihydroxy)borane 1 (21 - 27 mg, 0.10 - 0.12 mmol) was added to anhydrous pyridine or 2,6-di(tert-butyl)pyridine (0.2 -0.3 ml) at 20 °C. An exothermic reaction proceeded immediately and after 3 - 5 min. the quantitative formation of pentafluorobenzene was detected (¹⁹F NMR).

B. Aryl(dihydroxy)borane 3 (16 mg, 0.08 mmol) was dissolved in anhydrous pyridine (0.2 ml) at 20 °C. After 20 min. the ¹⁹F NMR spectrum showed the resonances of 3 (Table 2) and of 1,2,3,5-tetrafluorobenzene in the molar ratio of 4 : 1. 6 hours later only the polyfluoroaromatic product was present.

C. For kinetic measurements each of the fluorinated aryl(dihydroxy)boranes (1 - 8) (20 mg) was dissolved in pyridine (0.300 ml) and D₂O (0.030 ml) at 0 °C and placed into the probehead of the NMR spectrometer within 1 - 2 min. The measurements proceeded at 32 °C. For the high temperature series the NMR tube with the solution was kept at 100 ± 2 °C for the appropriate time, cooled immediately to 32 °C and the composition of the reaction mixture was determined by ¹⁹F NMR spectroscopy. The reaction rates were determined with an accuracy of 25 - 35 %.

D. Acid 1 (7 mg, 0.03 mmol) was dissolved in toluene (0.074 ml) and 2,6-di(tert-butyl)pyridine (63 mg, 0.33 mmol) was added to the solution at 20 °C. After 3 - 5 min. pentafluorobenzene was formed in quantitative yield (19F NMR).

Interaction of pentafluorophenyl(dihydroxy)borane (pentafluorophenylboronic acid) with K_2CO_3 in toluene.

Acid 1 (380 mg, 1.79 mmol) was stirred with K_2CO_3 (1 g) in toluene (2.5 ml) at 20 °C. After 18 h the conversion of 1 into pentafluorobenzene was 86 % and after 24 h 100 %.

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft, the Russian Foundation for Basic Research, and the Fonds der Chemischen Industrie.

References

 H.-J. Frohn, N. Y. Adonin, V. V. Bardin, V. F. Starichenko, Z. Anorg. Allg. Chem. submitted for publication.

- [2] Aldrich Katalog, Handbuch Feinchemikalien (Deutschland), 2000 - 2001, 674, 675 and 1488.
- [3] R. D. Chambers, T. Chivers, J. Chem. Soc. 1965, 3933.
- [4] E. Vedejs, R. W. Chapman, S. C. Fields, S. Lin, M. R. Schrimpf, J. Org. Chem. 1995, 60, 3020.
- [5] H.-J. Frohn, H. Franke, P. Fritzen, V. V. Bardin, J. Organomet. Chem. 2000, 598, 127.
- [6] B. M. Mikhailov, Y. U. Bubnov, Organoboron compounds in organic synthesis. /; Bell Bain, Glasgow, 1984.
- [7] Methoden der organischen Chemie (Houben-Weyl). Bd 13/3b. Organobor-Verbindungen II; Thieme, Stuttgart, 1983.
- [8] A. D. Ainley, F. Challenger, J. Chem. Soc. 1930, 2171.
- [9] H. G. Kuivila, J. F. Reuwer, J. A. Mangravite, Can. J. Chem. 1963, 41, 3081.
- [10] R. E. London, S. A Gabel, J. Am. Chem. Soc. 1994, 116, 2562.
- [11] H.-J. Frohn, N. Y. Adonin, V. V. Bardin, Main Group Metal Chemistry 2001, 24, 845.