

Investigation of Potassium Fluoride Supported on Alumina in the Deboronation of *o*-Carborane

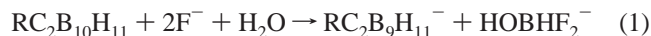
Thomas D. Getman

Department of Chemistry, Northern Michigan University,
Marquette, Michigan 49855

Received February 27, 1998

Introduction

The fluoride ion, typically in the form of NBu_4F , has been used in the deboronation of a variety of *closo*-carboranes.^{1,2} In the initial report,¹ attempts were made to exclude all water from the reactions; however, the authors noted the difficulty of ensuring the dryness of NBu_4F solutions. A subsequent study,² which addressed only *o*- and *m*-carborane³ derivatives, demonstrated that the exclusion of water was not necessary, and in fact, the presence of water was advantageous in the deboronation reaction. More recently it has been shown that 2 equiv of fluoride and 1 equiv of water are required to achieve complete deboronation according to eq 1.⁴



Although the use of fluoride to deboronate carboranes is a relatively new development, the fluoride ion has long been investigated as a potential base for a variety of synthetic organic reactions.⁵ In particular, the use of the fluoride ion to promote the *O*-alkylation of phenols and alcohols has been investigated in detail.^{6–8} Various combinations of fluoride salts supported on inorganic solids have been studied in relationship to these *O*-alkylation reactions^{7b} with potassium fluoride supported on alumina offering the best combination of stability, low degree of hygroscopic character, and low cost.

Given that potassium fluoride supported on alumina has proven to be an effective and inexpensive reagent in the *O*-alkylation reactions, we have set out to investigate if it would have similar benefits in the deboronation of *o*-carborane. Furthermore, if so, would the alumina adsorb the boron–fluorine species formed during the deboronation and thus allow the easy isolation of $\text{K}[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$?

Experimental Section

All ^1H , ^{13}C , and ^{11}B NMR spectra were obtained on a Varian Unity Inova spectrophotometer operating at 399.9, 100.6, and 128.3 MHz, respectively. Proton spectra were referenced to residual protons from

Table 1. Percentage of Deboronation of *o*-Carborane Achieved by the Use of KF/Alumina in “Wet” Solvent under Reflux Conditions as a Function of Solvent and Time^a

“wet” solvent	reaction time (h)	% deboronation
acetonitrile	23	100
glyme	44	94
tetrahydrofuran	100	63

^a 0.20 M *o*-carborane, 10:1 molar ratio F^-/o -carborane.

Table 2. Percentage of Deboronation of *o*-Carborane Achieved by the Use of KF/Alumina in Dry Solvent as a Function of Solvent, Time, and Reaction Temperature^a

dry solvent	reaction time (h)	temperature	% deboronation
acetonitrile	48	reflux	100
acetonitrile	19	reflux	48
acetonitrile	20	rt	17
glyme	24	rt	0

^a 0.20 M *o*-carborane, 10:1 molar ratio F^-/o -carborane.

the deuterated solvent (CD_3CN $\delta = 1.93$ ppm). Carbon-13 spectra were referenced to the ^{13}C resonance of the deuterated solvent ($\text{CD}_3\text{-CN}$, $\delta_{\text{CH}_3} = 1.3$ ppm, $\delta_{\text{CN}} = 118.2$ ppm). Boron-11 spectra were referenced to an external sample of $\text{B}_{10}\text{H}_{14}$ in C_6D_6 (*B*(2,4), $\delta = -36.5$ ppm). Infrared data were obtained on a Perkin-Elmer model 1600 Fourier transform infrared (FTIR) spectrometer either neat between CaF_2 plates or, for solid products, as KBr pellets.

Materials. *o*-Carborane, purchased from Dexsil Corp., was used as received. Solvents were purchased from Aldrich. Potassium fluoride dihydrate was purchased from Fisher Scientific Co. and used as received. Alumina (neutral, Brockman I) was purchased from Aldrich and used as received. The KF/alumina reagent was prepared according to the literature procedure.^{7b}

Deboronation Reaction. When dry solvent was employed, the solvent was dried according to published procedures.⁹ The deboronation was performed under a N_2 atmosphere, but the workup was performed in the open air. The following procedure was followed for the “wet” solvent deboronation experiments.

Deboronation of *o*-C₂B₁₀H₁₂ Using KF/alumina. In a typical experiment, a 10-mL round-bottom flask was loaded with *o*-carborane (54.0 mg, 0.374 mmol), KF/alumina (587.7 mg, 3.717 mmol fluoride ion), acetonitrile (2.0 mL), water (14 μL , 0.78 mmol), and a magnetic stir bar. The reaction mixture was refluxed with stirring for 24 h. The mixture was allowed to cool to room temperature and filtered, and the KF/alumina was washed with acetonitrile (~ 2 mL). The IR and ^{11}B NMR spectra of the combined filtrates were obtained.

In reactions where deboronation was not complete, integration of resonances from *o*-carborane and $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ in the $^{11}\text{B}\{^1\text{H}\}$ spectra were used to determine the approximate percentages of each species (Tables 1 and 2).

Isolation of $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3][\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$. Employing the above procedure, we deboronated *o*-carborane (111.1 mg, 0.7705 mmol). The acetonitrile was removed from the filtered reaction solution via an aspirator until the flask was no longer cool to the touch. A clear viscous solution was present. This solution was dissolved in water (~ 8 mL), and $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3]\text{Br}$ (286 mg, 0.801 mmol) that was dissolved in a minimum amount of water was added. A white precipitate immediately formed. The mixture was allowed to stand (~ 1 h), at which point the solid had settled and was filtered from the solution. The filter cake was washed with 3 10-mL portions of water, dried under suction for five minutes, and left to dry in the fume hood

(9) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall: Englewood Cliffs, NJ, 1970; pp 114–121.

- (1) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812–815.
- (2) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K.; Colquhoun, H. M. *Polyhedron* **1996**, *15*, 565–571.
- (3) The name *o*-carborane will be used throughout this paper to indicate 1,2-dicarbadodecaborane (12) and *m*-carborane will be used to indicate 1,7-dicarbadodecaborane (12).
- (4) Fox, M. A.; MacBride, J. A. H.; Wade, K. *Polyhedron* **1997**, *16*, 2499–2507.
- (5) Clark, J. H. *Chem. Rev.* **1980**, *80*, 429–452.
- (6) Miller, J. M.; So, K. H.; Clark, J. H. *Can. J. Chem.* **1979**, *57*, 1887–1889.
- (7) (a) Yamawaki, J.; Ando, T. *Chem. Lett.* **1979**, 755–758. (b) Ando, T.; Yamawaki, J.; Kawate, T.; Sumi, S.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2501–2507.
- (8) (a) Ishikawa, N.; Kitazume, T.; Nakabayashi, M. *Chem. Lett.* **1980**, 1089–1090. (b) Ishikawa, N.; Kitazume, T.; Yamazaki, T.; Mochida, Y.; Tatsuno, T. *Chem. Lett.* **1981**, 761–764.

overnight. The $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3][\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$ obtained was characterized by ^1H , ^{13}C , and ^{11}B NMR and IR spectroscopies (yield: 267 mg, 84%).

Results

The results of experiments investigating the use of KF/alumina to deboronate *o*-carborane are presented in Tables 1 and 2. For the reaction employing refluxing wet acetonitrile, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum indicated the only boron species present in solution is $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$, indicating 100% deboronation. The IR spectrum reveals an absorption at 2520 cm^{-1} and the absence of any absorption at 2575 cm^{-1} . Both spectral results indicate 100% conversion of *o*-carborane to $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$.

In addition to these experiments, a blank experiment was performed in which KF/alumina was added to wet acetonitrile and refluxed for 24 h. After workup of this blank experiment, a white hygroscopic solid was obtained. Use of this hygroscopic solid in a deboronation reaction of *o*-carborane (wet acetonitrile, 24 h, reflux) resulted in 12% deboronation of *o*-carborane. For comparison purposes, a reaction was performed utilizing $\text{KF}\cdot 2\text{H}_2\text{O}$ (wet acetonitrile, 21 h, reflux) which resulted in 14% deboronation of *o*-carborane.

Discussion and Conclusions

Initial experiments focused upon determining the best solvent and reaction conditions for the deboronation reaction. The results are presented in Table 1. It can be seen that acetonitrile proved to be the best solvent for achieving 100% deboronation in a reasonable amount of time. No boron species other than *o*-carborane or $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ were observed during any of the ^{11}B NMR studies of the filtered reaction solutions. Apparently, the boron-fluorine species produced during the deboronation are adsorbed by the alumina.

Since alumina adsorbed the boron-fluorine species, it seemed this procedure could lead to the isolation of pure $\text{K}[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$ after filtration and removal of the solvent. Attempts to isolate pure $\text{K}[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$ by distilling off the acetonitrile resulted in only a clear oil being obtained. However, pure $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3][\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$ was obtained in high yield by dissolution of the clear oil in water followed by precipitation of the $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]^-$ anion by addition of $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3]\text{Br}$.

Upon further investigation, it was found that a hygroscopic white solid is obtained from the reaction of the KF/alumina

reagent with refluxing wet acetonitrile. This hygroscopic solid prevented the direct isolation of pure $\text{K}[\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$. The possibility that this hygroscopic solid might be responsible for the enhanced rate of deboronation observed in acetonitrile was eliminated when only 12% deboronation of *o*-carborane was achieved with this material. The identity of this hygroscopic solid has not been conclusively determined; however, it has been shown by IR analysis to contain some acetamide formed by the hydrolysis of the acetonitrile. The observation that acetamide does not deboronate *o*-carborane, and yet the hygroscopic solid does, implies that some fluoride ion has been released from the alumina. This implication is supported by the fact that potassium fluoride dihydrate results in a similar amount of deboronation (14%) compared to that observed with the hygroscopic solid (12%).

Additionally, due to the resurgence of interest in the organic chemistry of compounds possessing borane and carborane groups,^{10,11} the deboronation of *o*-carborane under conditions normally employed in the O-alkylation of alcohols and phenols was investigated. The results are presented in Table 2. It has been found^{7b} that the O-alkylation of alcohols and phenols using KF/alumina proceeds most quickly when acetonitrile or glyme are used as the solvent. Therefore, it is clear from the data of Table 2 and ref 7b that if an O-alkylation is to be performed in the presence of an *o*-carborane group without any deboronation, then glyme would be the solvent of choice.

In conclusion, this study has shown that if the fluoride ion is the base of choice for deboronating an *o*-carborane, then KF/alumina is an effective and inexpensive reagent. Its advantages over tetrabutylammonium fluoride include lower cost (approximately one-eighth the cost per reaction performed) and the ability to vary the cation as demonstrated by the isolation of $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3][\text{nido-7,8-C}_2\text{B}_9\text{H}_{12}]$.

Acknowledgment. I thank Mr. Jerry Lutz of Michigan Technological University for the acquisition of NMR data on a Varian Unity Inova instrument funded in part by NSF CHE-9512445. I also thank Northern Michigan University for support of this work through the faculty research grant program. Finally, I thank Ms. Carolyn McManis for her helpful suggestions during the proofreading of the manuscript.

IC980222M

(10) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950–984.

(11) Gabel, D. *Stud. Med. Chem.* **1996**, *1*, 239–270.