## Communication

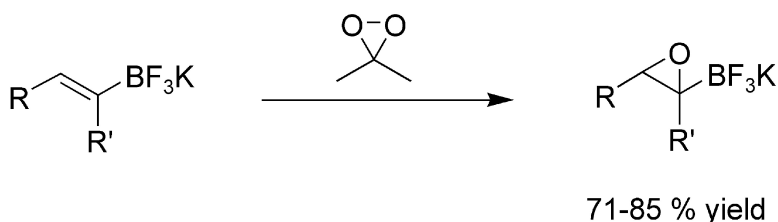# Expanding Organoboron Chemistry: Epoxidation of Potassium Organotrifluoroborates

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71-85 % yield

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# Expanding Organoboron Chemistry:  Epoxidation of Potassium Organotrifluoroborates

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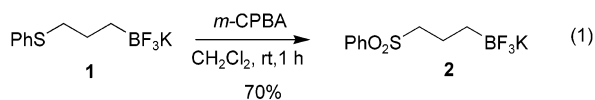
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Organoboron compounds have had a profound impact on organic synthesis.[1] Their unique reactivity has made them among the most versatile organometallic intermediates for the construction of organic molecules.[2] In many synthetic methods based on organoborons, oxidation of the carbon−boron bond[3] has been used as a key step for further or final transformations. However, given the power of modern oxidations to incorporate functionality selectively into organic substrates,[4] the incompatibility of most oxidants with organoboron compounds[5] can be regarded as a significant limitation because it severely restricts the ability to modify the organic moiety while retaining the valuable carbon−boron bond.

There are few reports of organic functionality being oxidized in the presence of organoboron compounds wherein the carbon−boron bond remains intact.[6] In this communication, we describe our initial efforts toward oxidative transformations with potassium organo-trifluoroborates ($RBF_3K$) that lead to interesting materials in which the carbon−boron bond is retained.

Organotrifluoroborate salts have emerged as a new class of air-stable boron derivatives, facile to prepare in high yields and purities,[7] easy to handle, and feasible to utilize in a number of useful synthetic processes (e.g., Suzuki reactions,[8,9] rhodium-catalyzed 1,4-additions,[10] and allylation of aldehydes[11]).

As part of an ongoing program in organoboron research,[9] we were pleased to discover that the conventional oxidation of a thioether to a sulfone with *m*-CPBA could be performed in the presence of a pendant alkyltrifluoroborate. Thus, potassium 3-phenylthiopropyltrifluoroborate $1$[12] was treated with 2 equiv of *m*-CPBA in $CH_2Cl_2$ at room temperature, and after 1 h the phenylsulfonylpropyltrifluoroborate $2$ precipitated from the reaction mixture (eq 1). Thus, the trifluoroborate moiety not only withstood the oxidative conditions of the peracid, but the acidic conditions of the carboxylic acid byproduct as well.

$$PhS\diagup\diagdown\diagup BF_3K \quad \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ rt,1 h}]{m\text{-CPBA}} \quad PhO_2S\diagup\diagdown\diagup BF_3K \quad (1)$$

**1**      **2**

70%

In view of the unprecedented stability of the potassium alkyl-trifluoroborate with peracids,[5] we pursued the possibility that related boron derivatives might also be stable under other oxidative conditions. One of the most studied oxidation processes is the epoxidation reaction.[13] Indeed, oxiranes are widely utilized as versatile synthetic intermediates, and the epoxide functional group is also found in a number of interesting natural products.[14] Among the epoxidation reagents that we have investigated,[15] dimethyl-dioxirane[16] is uniquely effective. We were delighted to find that the reaction of potassium *trans*-1-dec-1-enyltrifluoroborate[9c] $3a$ with 1.2 equiv of dimethyldioxirane at room temperature led to clean and quantitative generation of the epoxytrifluoroborate $4a$ (Table 1, entry 1).[17] [1]H, ^{13}C, ^{19}F, and [11]B spectroscopy corroborated the

**Table 1.** Epoxidation of Potassium Organotrifluoroborates with Dimethyldioxirane (0.05 M Solution in Acetone)

| entry | organotrifluoroborate | product | % isolated yield[a] |
|-------|----------------------|---------|---------------------|
| 1 | $C_8H_{17}$⌒BF$_3$K  **3a** | $C_8H_{17}$⌒epoxide⌒BF$_3$K  **4a** | 85 |
| 2 | Ph⌒BF$_3$K  **3b** | Ph⌒epoxide⌒BF$_3$K  **4b** | 70[b] |
| 3 | Cl⌒BF$_3$K  **3c** | Cl⌒epoxide⌒BF$_3$K  **4c** | 71 |
| 4 | BF$_3$K / Me  **3d** | epoxide BF$_3$K / Me  **4d** | 80 |
| 5 | ⌒⌒BF$_3$K  **5** | epoxide⌒⌒BF$_3$K  **6** | 70 |

*[a]* >95% conversion by ^{1}H NMR. *[b]* Reaction was performed at −78 °C.

formation of the epoxide and the retention of the trifluoroborate moiety.[12] The potassium epoxytrifluoroborate $4a$ was obtained as a white solid, completely stable in the air.

This epoxidation has proved to be efficient with an array of potassium alkenyltrifluoroborates.[9c] The reaction of the *trans*-styryltrifluoroborate $3b$ occurs at −78 °C almost instantaneously (entry 2). Other partners, such as *trans*-3-chloropropenyl tri-fluoroborate $3c$ (entry 3) or 1,1-disubstituted olefin $3d$ (entry 4), efficiently afford the desired oxiranyltrifluoroborates. All of the products were isolated as air-stable white solids. The stability of the epoxytrifluoroborates is particularly amazing, given their structural analogy to oxiranyl anions,[18] which are known to be extraordinarily unstable. The covalent nature of the C−B bond thus prevents the detrimental α-elimination process characteristic of most oxiranyl anions. Furthermore, the strong B−F bonds of the tetra-coordinate trifluoroborate not only provide mechanistic resistance against oxidation and protonolysis reactions normally associated with organoboranes but clearly prevent the well-recognized α-trans-fer reaction at the labile epoxide as well.[1,2]

In further studies, we have examined the epoxidation process with a potassium ω-alkenyltrifluoroborate. Exposure of potassium 3-butenyltrifluoroborate $5$[12] (easily obtained from the corresponding Grignard derivative)[19] with dimethyldioxirane gave the desired potassium epoxyethyl trifluoroborate $6$ in 70% yield after crystallization (entry 5).

Suzuki−Miyaura reactions[20] wherein an epoxide resides within the same coupling partner as the boron moiety[21] are rare and not well documented.[22] Thus, with the potassium oxiranylethyltri-fluoroborate $6$ in hand we conducted a cross-coupling reaction with

**Scheme 1**
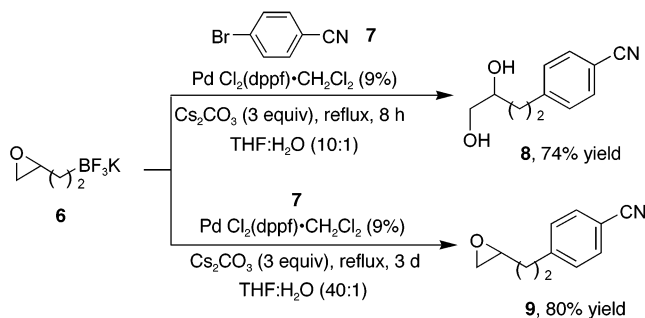


4-cyanophenyl bromide **7** as the electrophile. The previously reported conditions found to be optimal for Suzuki coupling of potassium alkyltrifluoroborates[9a] [PdCl$_2$(dppf)·CH$_2$Cl$_2$ (9 mol %), Cs$_2$CO$_3$ (3 equiv) as base, heated at reflux in THF:H$_2$O (10:1)] afforded the 4-cyanophenyl-1,2-butanediol **8** with a 74% yield after column chromatography. Although this type of cross-coupling/ring-opening process is of interest, more importantly we could perform the desired Suzuki reaction and retain the epoxide by simply decreasing the amount of the water in the solvent mixture (THF: H$_2$O) to a 40:1 ratio, isolating the purified epoxyethylaryl compound **9** in 80% yield (Scheme 1).

In summary, we have found that potassium organotrifluoroborates possess a reactivity that is complementary to other organoboron compounds, permitting olefin epoxidation with dimethyldioxirane with concomitant retention of the carbon–boron bond. This work thus represents a significant expansion in the chemistry of organoboron compounds. We have described the first potassium $\alpha,\beta$-epoxytrifluoroborates, compounds that could have interesting reactivity in analogy to the chemistry of oxiranyl anions. In addition, we have successfully accomplished the first well-documented *B*-alkyl Suzuki–Miyaura cross-coupling reaction with an epoxy-alkyltrifluoroborate derivative. Studies directed toward the use of $\alpha,\beta$-epoxytrifluoroborates as oxiranyl anion equivalents as well as the exploration of other oxidative processes of organotrifluoroborates are under investigation.

**Supporting Information Available:** Experimental procedures, compound characterization data, and NMR spectra of **1**, **2**, **4(a**–**e)**–**9** (PDF). This material is available free charge via the Internet at http://pubs.acs.org.

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(15) Epoxidation using *m*-CPBA also affords the epoxide **3a** with excellent conversion, but the product crystallizes together with *m*-chlorobenzoic acid. Attempts to perform a biphasic media reaction with a solution of NaHCO$_3$ afforded decanal, probably as a consequence of the aqueous basic hydrolysis of the B–F bond in the trifluoroborates (see ref 9a) to a boronic acid or borate that under the peracid conditions affords the enol leading to the aldehyde. Other oxidizing agents such as Davis's oxaziridine or amine *N*-oxides leave the starting alkenyltrifluoroborate intact.

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(23) In the absence of water, starting aryl bromide **7** was recovered along with its homocoupling product in a 1:1 ratio.

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