A Qualitative Analysis of a "Bora-Brook Rearrangement": The Ambident Reactivity of Boryl-Substituted Alkoxide Including the Carbon-to-Oxygen Migration of a Boryl Group

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Ⓢ *Supporting Information*

ABSTRACT: A bora-Brook rearrangement, i.e., the migration of boryl group from a carbon to an oxygen atom in an isolated α-boryl-substituted alkoxide, was examined, and decisive factors for the acceleration of this reaction are disclosed. In this rearrangement, the boryl-substituted alkoxide exhibited ambiphilic reactivity toward electrophiles to afford two types of products, which are electrophiles bound either at the oxygen or at the carbon atom. Using polar solvents, a saturated backbone of the boron-containing heterocycle, or larger alkali metal cations resulted in a significantly increased reaction rate of base-catalyzed isomerization of α-borylbenzyl alcohol including the bora-Brook rearrangement.

■ INTRODUCTION

The Brook rearrangement describes the migration of a silyl group from a carbon to an anionic oxygen atom in an alkoxide, which results in the formation of a carbanionic intermediate.[1] Such reactions are classified according to the chain length between the carbon and oxygen atoms that are involved in the migration, and they are consequently labeled [1,n]-Brook rearrangements, in which n refers to the number of carbon atoms between silicon and oxygen in the starting alkoxide (eq 1).[2] The Brook rearrangement is initiated by the formation of

$$\text{O}^- \overset{}{\underset{\text{CH}_2}{\bigvee_{n-1}}} \xrightarrow[\text{rearrangement}]{[1,n]\text{-Brook}} \text{SiR}_3 \quad \text{O} \overset{}{\underset{\bar{\text{C}}\text{H}_2}{\bigvee_{n-1}}} \quad \text{(Eq. 1)}$$

five-coordinate silicate intermediate that is generated from the attack of the alkoxide to the low-lying σ^* orbital of the Si−X bond. The driving force for Brook rearrangements depends on the balance between bond energy values (Si−C = 76 kcal/mol; Si−O = 108 kcal/mol)[3] and the higher stability of the oxyanion relative to that of the carbanion.[1] The Brook rearrangement is an umpolung-type reaction, which is characterized by its high stereoselectivity and stereospecificity, features that have made it a highly popular tool in the area of synthetic organic chemistry.[4]

Boron-containing compounds have a well-established track record as Lewis acidic reagents in organic chemistry, due to the vacant p-orbital on the boron center.[5] Considering the

aforementioned features of the Brook rearrangement, boron-containing compounds should be expected to display a similar reactivity. Although we are not aware of any report on the "direct" observation of a bora-Brook rearrangement, indirect evidence has been presented in the reaction of α-borylbenzyl alcohol with an (IPr)Cu-Me, which led to the formation of a rearranged (boryloxybenzyl)copper complex in favor of the expected (α-borylbenzyloxy)copper complex (eq 2).[6] Subsequent theoretical studies by Lin and Marder suggested that the (α-borylalkyloxo)copper complex should be able to undergo a rearrangement to furnish the (α-boryloxyalkyl)copper complex through an annular three-membered transition state (eq 3).[6,7] A similar rearrangement via an annular three-membered transition state was suggested by Matteson for the conversion of $HOCH_2B(OH)_2$ to $CH_3OB(OH)_2$ by treatment with water under basic conditions (eq 4).[8,9] Additionally, one may suspect that the bora-Brook rearrangement could be one of the reasons why the attempted *O*-benzylation of an α-Bpin-substituted alcohol afforded a low yield under highly basic conditions (eq 5, right),[10] although no information was provided regarding the side products. Instead, the *O*-protection proceeded in high yield under mildly basic conditions with a highly oxophilic silyl reagent (eq 5, left). The *O*-acylation of an alcohol bearing an sp[3]-hybridized trifluoroborate substituent proceeded in high yield under highly basic conditions (eq 6),[11] which implies that

(Eq. 2)


(Eq. 3)

(Eq. 4)

(Eq. 5)

(Eq. 6)

the existence of a vacant p-orbital at the boron atom should play a significant role in lowering the yield of the O-benzylated product in eq 5.

We have recently reported the synthesis and studies on the reactivity of boryllithium compounds that are anionic and nucleophilic.[12] In one of these studies,[12g] boryllithium **1a** bearing a saturated five-membered ring was found to afford hydroxyborane **3a** from the reaction with CO_2, while the expected carboxylic acid derivative (**2a**) was not observed. Conversely, boryllithium **1b** with unsaturated five-membered ring furnished **2b** as the major product together with minor amounts of **3b** (Scheme 1). The formation of **3a,b** may be explained by the protonation of **6a,b**, which could be generated from **4a,b** and **TS5a,b** after loss of CO, a notion that is consistent with previous reports by Sadighi, Lin, and Marder.[6,7,13] The difference in reactivity between **1a** and **1b** may be explained in terms of a destabilization of **TS5b** due to

Scheme 1. Reaction of Boryllithium Compounds 1a,b with CO_2[a] and the Proposed Mechanism for the Formation of 6a,b
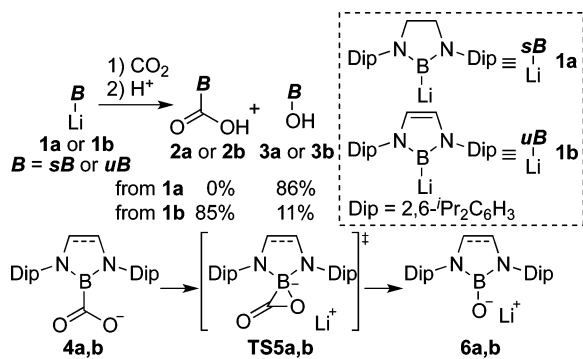
[a]**a**: saturated C—C backbone. **b**: unsaturated C=C backbone of the five-membered boron-containing heterocycle.

the dearomatization of the five-membered boron-containing heterocycle. Even though the bora-Brook rearrangement may proceed along various pathways, as described in the previous paragraph, a qualitative understanding of this rearrangement still remains elusive. In order to shed light on this rather unexplored topic, we decided to investigate the fundamental features of the bora-Brook rearrangement. Herein, we report the ambident reactivity of isolated α-borylalkoxides via the bora-Brook rearrangement. Moreover, we present the effects of solvent polarity, structure of the boryllithium backbone, and size of the alkali metal cation on the reaction rate.

■ RESULTS AND DISCUSSION

Reaction of **1a** with benzaldehyde in THF at −78 °C, followed by a protonation with Et$_3$N·HCl at room temperature, furnished a mixture of α-borylbenzyl alcohol **7a** and its isomeric alkoxyborane **8a**, in which the rearranged **8a** is the major product (Scheme 2).[14] The identity of **8a** was confirmed

Scheme 2. Reaction of 1a with Benzaldehyde Followed by Protonation
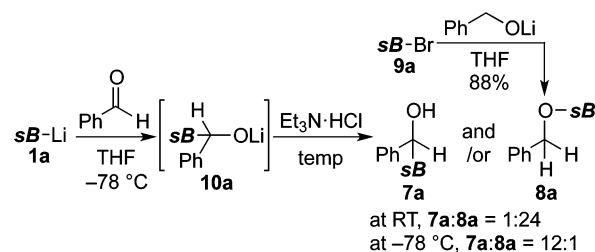
by comparison with an independently synthesized sample of **8a**, which was obtained from bromoborane **9a** and potassium benzyloxide. In contrast, quenching the reaction between **1a** and benzaldehyde in THF at −78 °C afforded **7a** as the major product. The formation of these two products may be explained in terms of an ambident reactivity of alkoxide intermediate **10a**, which should be generated from the nucleophilic attack of **1a** toward benzaldehyde.

In order to confirm this hypothesis, we tackled the isolation of intermediate **10a**. Treatment of boryl-substituted benzyl alcohol **7a** with ^{n}BuLi in n-hexane afforded alkoxide (**10a**)$_2$ (Scheme 3), whose dimeric structure was confirmed by an X-

Scheme 3. Isolation of Lithium α-Borylbenzyl Alkoxide Intermediate (10a)$_2$
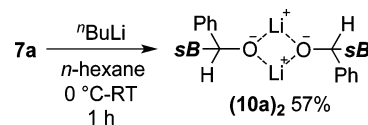
ray diffraction study carried out on a single crystal grown from toluene solution. Figure 1 displays the molecular structure of (**10a**)$_2$·toluene, which crystallizes in the achiral space group C_2/c and contains an identical number of centrosymmetric R,R- and S,S-dimers in its crystal lattice. The dimeric structure arises from the presence of a $[Li_2O_2]$ core, which exhibits Li—O bonds of slightly different length, a phenomenon that has previously been reported for a similar lithium phenoxide dimer.[15] In addition, one of the two Dip benzene rings intermolecularly coordinated to Li$^+$. Single crystals of (**10a**)$_2$· THF, obtained from a THF solution, exhibited an identical
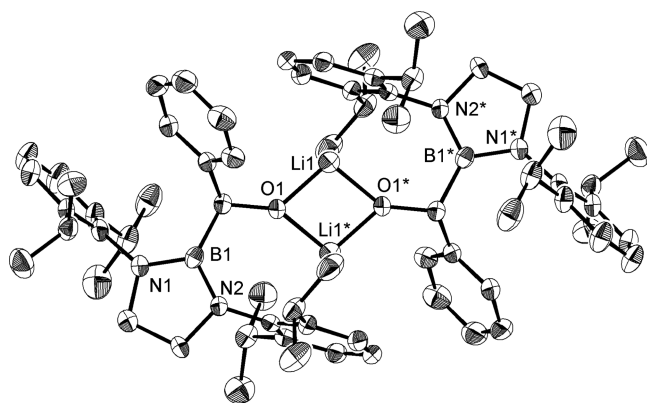
Figure 1. Molecular structure of (**10a**)$_2$·toluene (atomic displacement parameters set at 50%; one half of the dimer represents the asymmetric unit of the crystal, which is denominated by the atomic labels without asterisks; all hydrogen atoms and the cocrystallized toluene molecule are omitted for clarity).

dimeric structure (see the Supporting Information). The ^{1}H NMR spectrum of a C$_6$D$_6$ solution of (**10a**)$_2$ suggested the formation of a diastereomeric mixture of the homo- (*R,R* and *S,S*) and heterodimers (*R,S* and *S,R*). The ^{11}B NMR spectrum of (**10a**)$_2$ in C$_6$D$_6$ or THF-d_8 showed a broad resonance at δ_B = 28, which indicates that the boron atom retains its sp^2 configuration in these solvents. The observed high-field shifted ^{7}Li NMR resonances (δ_{Li} = −3.1 in C$_6$D$_6$, δ_{Li} = −2.1 in THF-d_8) for (**10a**)$_2$ are indicative for a persisting arene–Li$^+$ interaction in both solvents.[16] This result is in stark contrast to other solvated lithium alkoxide dimers (in ether, THF, TMEDA, or phosphine oxide solvates), which generally show moderately positive ^{7}Li NMR shifts.[17]

The reactivity of (**10a**)$_2$ toward electrophiles is ambient (Table 1). Treatment of (**10a**)$_2$ with Et$_3$N·HCl in C$_6$D$_6$ at

Table 1. Reactivity of (10a)$_2$ toward Several Electrophiles
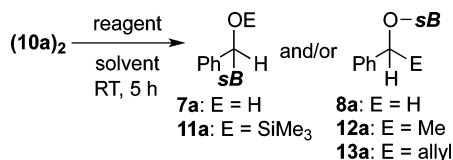
run	reagent	solvent	products (yield)^a
1	Et$_3$N·HCl	C$_6$D$_6$	**7a** (97%), **8a** (1%)
2	Et$_3$N·HCl	THF-d_8	**7a** (21%), **8a** (73%)
3^b	Me$_3$SiCl	C$_6$D$_6$	**11a** (69%), **7a** (<1%),^{c} (**10a**)$_2$ (27%)
4	Me$_3$SiCl	THF-d_8	**11a** (76%), **8a** (4%)^c
5	MeI	C$_6$D$_6$	no reaction
6	MeI	THF-d_8	**12a** (93%), **8a** (4%)^c
7	allylBr	C$_6$D$_6$	no reaction
8	allylBr	THF-d_8	**13a** (84%), **8a** (3%)^c

^{a}Estimated by ^{1}H NMR. ^{b}*t* = 52 h. ^{c}These compounds were probably generated by the reaction with protic impurities in the reagent.

room temperature resulted in the generation of *O*-protonated **7a** as the major product (run 1). Conversely, when the same reaction was carried out in THF-d_8, *C*-protonated **8a** was obtained as the major product (run 2). Reactions of (**10a**)$_2$ with Me$_3$SiCl in C$_6$D$_6$ and THF-d_8 afforded *O*-silylated **11a** as the only silylated product, together with several protonated byproducts (runs 3 and 4). It is noteworthy that the reaction in

C$_6$D$_6$ was much slower than that in THF-d_8. Treatment of (**10a**)$_2$ with relatively soft electrophiles such as MeI or allyl bromide in C$_6$D$_6$ did not induce any reactions (runs 5 and 7). On the contrary, when these reactions were carried out in THF-d_8, the major products obtained were *C*-functionalized **12a** and **13a** (runs 6 and 8). The formation of B–C bonds in **7a** and **11a**, as well as B–O bonds in **8a**, **12a**, and **13a**, was unambiguously confirmed by single-crystal X-ray diffraction analyses (see the Supporting Information). The complete structural characterization of all *O*- or *C*-functionalized products thus corroborated the ambient character of α-borylbenzyl alkoxide (**10a**)$_2$, which depends on the electrophile. This ambient behavior closely resembles the reactivity of α-silylalkoxide derivatives that undergo reversible Brook rearrangements.[18] The selectivity for the *O*- or *C*-functionalization products may be explained in the same terms that are used to account for the reactivity of other ambident anions,[19] namely, the *O*-anion and *C*-anion were under rapid equilibrium to each other, and either of the anions, kinetically favored by the charge or orbital control, underwent the reaction with the electrophile. Therefore, it is feasible to interpret the present reaction as a "bora-Brook rearrangement".

Subsequently, we carried out a kinetic study in order to examine the characteristics of the bora-Brook rearrangement. According to the ^{1}H NMR analysis, gentle heating of α-borylbenzyl alcohol **7a** in C$_6$D$_6$ in the presence of a catalytic amount of ^{n}BuLi led to the quantitative formation of alkoxyborane **8a** (Scheme 4).

Scheme 4. Base-Catalyzed Conversion of α-Borylbenzyl Alcohol 7a to 8a via a Bora-Brook Rearrangement
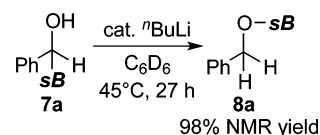
As the overlapping signals prevented the determination of the initial rate for the consumption of **7a** by ^{1}H NMR, para-fluorinated α-borylbenzyl alcohols **14a,b** were prepared to monitor the reaction by ^{19}F NMR. The addition of a catalytic amount of ^{n}BuLi to **14a,b** led, as in the case of **7a**, to the quantitative formation of alkoxyboranes **15a,b** (Table 2). Considering that the Brook rearrangement can also be catalyzed by bases,[20] the present reaction may also proceed via a deprotonation of alcohols **14a,b** to form alkoxides **16a,b**, followed by a bora-Brook rearrangement from alkoxides **16a,b** to carbanion intermediates **17a,b**, and a deprotonation of alcohols **14a,b** by **17a,b** to regenerate alkoxides **16a,b**. Considering the irreversible deprotonation of alcohols **14a,b** by carbanions **17a,b** to form alkoxyboranes **15a,b**, the bora-Brook rearrangement should also be irreversible under these proton-transfer conditions, in contrast to the reactions in Table 1. Furthermore, the reaction rate for the consumption of alcohols **14a,b** should be approximately equal to the reaction rate from **16a,b** to **17a,b**, due to the rapid deprotonation of the alcohol by the carbanion. The consumption of **14a,b** was monitored by ^{19}F NMR under various conditions in order to estimate the initial reaction rates of the bora-Brook rearrangement with saturation kinetics (Table 2).[21] The observed pseudo-first-order rate constant for the consumption of **14a** was essentially identical in toluene-d_8 and in THF-d_8, despite

Table 2. Kinetic Analysis of the Bora-Brook Rearrangement under Variable Conditions
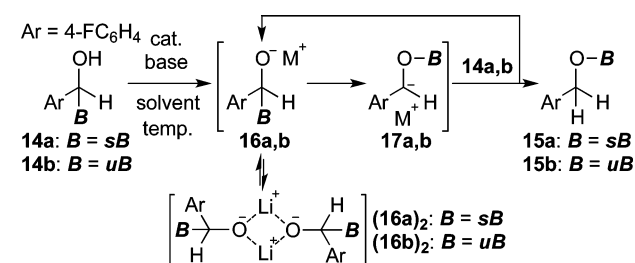
run	sub.	base	solvent	temp (°C)	result
1	14a	^nBuLi	toluene-d_8	85	$k_{obs} = 3.45 \times 10^{-4}$
2	14a	^nBuLi	THF-d_8	−50	$k_{obs} = 3.47 \times 10^{-4}$
3	14a	^nBuLi	toluene-d_8	80	$k_{obs} = 2.08 \times 10^{-4}$
4	14b	^nBuLi	toluene-d_8	80	$k_{obs} = 3.76 \times 10^{-5}$
5	14b	LiHMDS	C_6D_6	22	most of 14b recovered[a]
6	14b	NaHMDS	C_6D_6	22	quant. formation of 17b[a]
7	14b	KHMDS	C_6D_6	22	quant formation of 17b[a]

[a]Estimated by ^{1}H NMR

the substantial difference in reaction temperature ($\Delta T = 135$ °C) (runs 1 and 2). This result suggests that the bora-Brook rearrangement is most likely facilitated by the coordination of a molecule of THF to the lithium cation, which should enhance the nucleophilicity of the anionic oxygen atom. We also confirmed that alcohol 14a, which contains a saturated backbone, was consumed faster relative to 14b, which bears an unsaturated backbone (runs 3 and 4). This result is consistent with Scheme 1, as the lack of aromaticity in the boron-containing heterocycle of 14a should contribute to an increased reaction rate on account of an energetically lower transition state. The reaction rate was also affected by the countercation of the added base (runs 5−7). The addition of a catalytic amount of LiHMDS to 14b in C_6D_6 afforded merely trace amounts of 17b after 10 min at room temperature, whereas the use of NaHMDS or KHMDS immediately led to the quantitative formation of 17b. This result clearly indicates that the size of the cation has a strong impact on the reaction rate, whereby larger cations increase the nucleophilicity of the anionic oxygen atom. Although the labile coordination of solvents in the transition state prevented us from ascertaining its exact structure, one can easily imagine that the theoretically proposed cyclic three-membered transition state should be sensitive to the accelerating factors determined in this study (Figure 2).
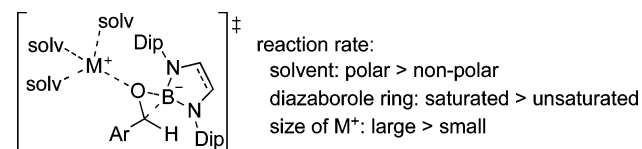

Figure 2. Effects of solvent, π-bonding in the diazaborole ring, and size of the alkali metal cation on the reaction rate based on the model consistent with the previously proposed cyclic three-membered-ring transition state.

CONCLUSION

In summary, we have experimentally validated the properties of the bora-Brook rearrangement, which consists of the migration of a boryl group from a carbon to an oxygen atom in boryl-substituted alkoxides. The α-borylbenzyl alkoxide dimer $(10a)_2$ was isolated as the intermediate, and the ambident reactivity of $(10a)_2$ manifested in its behavior toward electrophiles, which afforded either oxygen- or carbon-functionalized products, depending on the solvent and the electrophile. The bora-Brook rearrangement was accelerated in polar solvents, by diazaboroles with a saturated backbone, and by larger alkali metal cations. The unique reactivity of organoboron compounds disclosed herein will allow the development of new synthetic tools for organic chemistry in the future.

ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00283.

    Experimental details (PDF)
    Crystallographic data (CIF)

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Notes
The authors declare no competing financial interest.

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(21) Thermally labile alkoxide intermediates (**16a**)$_2$ and (**16b**)$_2$ were prepared independently from the reaction of **14a** and **14b** with ^{n}BuLi, and their structures were tentatively assigned on the basis of NMR measurements.