



## Deoxygenation of benzylic alcohols using chloroboranes

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### ABSTRACT

New boron-based methods for deoxygenating benzylic alcohols via the corresponding alkoxides are reported.

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In 1992, Eisch reported the stepwise deoxygenation of secondary benzylic alcohols via a diisobutylaluminum alkoxide intermediate (Scheme 1).<sup>1</sup> In this transformation,  $\text{AlBr}_3$  is used to coordinate an aluminoxane center that contains a hydride source ( $\text{Al-H}$ ). The use of a hydroalumination promoter ( $\text{Cp}_2\text{TiCl}_2$ ) is essential.

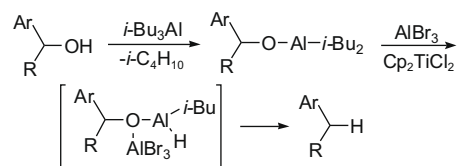
Later, Baba's group discovered an  $\text{InCl}_3$ -catalyzed deoxygenation of secondary and tertiary alcohols using chlorodiphenylsilane as the hydride source.<sup>2</sup> The reaction proceeds through a hydrodiphenylsilyl ether intermediate ( $\text{R}_1\text{R}_2\text{CH-O-SiPh}_2\text{H}$ ). Due to the low Lewis acidity of silicon, addition of  $\text{InCl}_3$  is necessary to facilitate both the C–O bond cleavage and the hydrogen migration from silicon to carbon.

In recent years, we discovered the transition-metal-free coupling of alkoxides with halovinylboron dihalides<sup>3</sup> and alkynylboron dichlorides<sup>4</sup> under very mild reaction conditions (Scheme 2). From the point of view of organic synthesis, these reactions provide unprecedented routes for replacing hydroxyl groups with stereodefined halovinyl and alkynyl groups. In all these reactions, migration of either a vinyl or an alkynyl group from a boron atom to a carbon center was involved. Notably, the heightened Lewis acidity of the boron center in alkoxyboron halide intermediates permits the migration to proceed smoothly without the addition of extra Lewis acids. A recent mechanistic investigation<sup>5</sup> revealed that this migration most probably proceeds via a carbocation pathway.

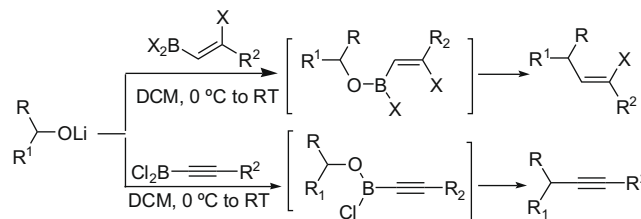
Encouraged by these results, we postulated that a hydrogen migration in an intermediate such as **1** (generated by simply mix-

ing an alkoxide with dichloroborane) should also be feasible (Scheme 3). In this case, dichloroborane would act as both Lewis acid and hydride source. The method would provide a new route to diarylmethane derivatives<sup>6,7</sup> which are important in pharmaceutical,<sup>8</sup> dye,<sup>9</sup> and material<sup>10</sup> chemistry.

As shown in Table 1, the new deoxygenation reaction proceeds efficiently at room temperature to offer products in moderate to high yields. Ether and halo groups survive the weakly Lewis acidic reaction conditions although, in a few cases (entries 9 and 13),



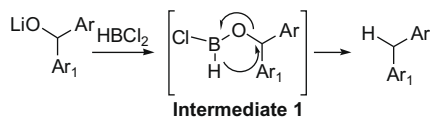
**Scheme 1.** Stepwise deoxygenation via diisobutylaluminum alkoxide intermediates.



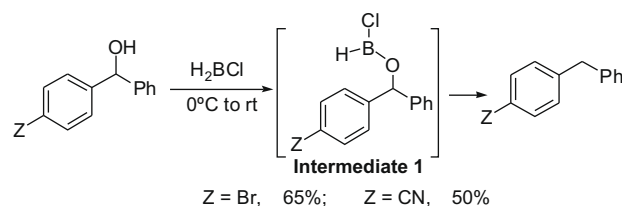
**Scheme 2.** Coupling of alkoxides with vinyl- and alkynylboron dichlorides.

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**Scheme 3.** Deoxygenation of alkoxides using dichloroborane.



**Scheme 6.** Deoxygenation of alcohols using monochloroborane.

**Table 1**  
Deoxygenation through alkoxide using  $\text{HBCl}_2^a$

Entry	R	Y	Z	Yield <sup>b</sup> (%)
1	H	H	H	63
2	H	<i>p</i> -Cl	H	67
3	H	<i>p</i> -F	<i>p</i> -F	70
4	H	<i>p</i> -Me	H	82
5	H	<i>o</i> -OMe	H	84
6	H	<i>p</i> -OMe	<i>p</i> -OMe	72 (95) <sup>c</sup>
7	H	H	3,4,5-(OMe) <sub>3</sub>	79
8	H	H	<i>p</i> -NO <sub>2</sub>	58
9	H	H	<i>p</i> -OBn	65 <sup>d</sup> (78) <sup>e</sup>
10	H	H	<i>p</i> -OMOM	76 <sup>e</sup>
11	Ph	H	H	96
12	Me	H	H	94
13	H	— <sup>f</sup>	H	56 <sup>g</sup>

<sup>a</sup> All reactions were carried out on a 1.5 mmol scale.

<sup>b</sup> Isolated yield.

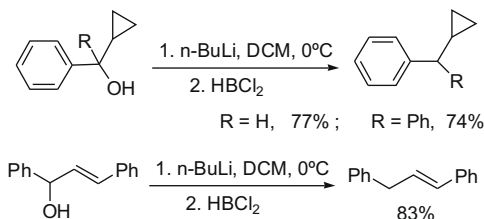
<sup>c</sup>  $\text{H}_2\text{BCl}$  was used in place of  $\text{HBCl}_2$ .

<sup>d</sup> A 12% yield of diarylchloromethane was isolated.

<sup>e</sup> The MOM group was cleaved during reduction.

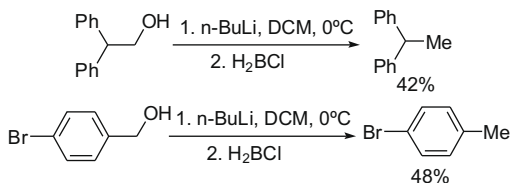
<sup>f</sup> 9-hydroxyfluorene was used as starting material.

<sup>g</sup> A 21% yield of 9-chloro-9H-fluorene was isolated.



**Scheme 4.** Deoxygenation of alkoxides using dichloroborane.

chlorinated by-products may form. In previously reported methods for deoxygenating secondary alcohols (including lithium–ammonia,<sup>11</sup> sodium borohydride–trifluoroacetic,<sup>12</sup> zinc iodide–sodium cyanoborohydride,<sup>13</sup> indium trichloride–chlorodiphenylsilane,<sup>2</sup> hypophosphorus–iodine,<sup>14</sup> and  $\text{Mo}(\text{CO})_6$ –Lawesson's reagent<sup>15</sup>), ether cleavage and hydrogenolysis of halogen atoms are common side reactions due to either high acidity or the use of strongly reducing conditions.



**Scheme 5.** Deoxygenation of primary alkoxides using monochloroborane.

The new deoxygenation also works well for benzylic alcohols bearing a cyclopropyl group (Scheme 4). The tolerance of the cyclopropyl group indicates that the reaction most probably proceeds through a concerted reaction mechanism rather than through a carbocation intermediate. In addition, vinyl groups are stable under the reaction conditions.

As noted in entries 9 and 13 (Table 1), the deoxygenation reaction can lead to undesired chlorinated by-products. Therefore, we examined the possibility of using  $\text{H}_2\text{BCl}$  in the place of  $\text{HBCl}_2$  which would result in the formation of an alkoxide intermediate bearing only hydrogen atoms on the boron attached to the oxygen. This modification successfully inhibited the formation of the chlorinated by-product, entry 9. Little improvement was noted in reactions using 9-hydroxyfluorene. However, the deoxygenation of primary alcohols using  $\text{H}_2\text{BCl}$  is remarkable though the reactions produce only moderate yields (Scheme 5).

We also examined the possibility of generating intermediate 1 by mixing benzylic alcohols with monochloroborane (Scheme 6). This would obviate the use of butyllithium and could be beneficial when certain functional groups (–Br and –CN) are present. The direct reaction produces the desired products in moderate yields.

In conclusion, new boron-based deoxygenation methods for converting benzylic alcohols to diarylmethanes are reported. The deoxygenation of alkoxides using dichloroborane not only expands our knowledge in organoboron dihalide chemistry but also provides evidence helpful in understanding the importance of Lewis acidity in previously reported deoxygenation methods.

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