

# Synthesis of Alkylarylcarbinols via the Reaction of Organoboranes with Arylmethyl Chlorides

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( $\alpha$ -Chloroaryl)methyl anions, generated *in situ* by the deprotonation of arylmethyl chlorides with dicyclohexylamide, readily react with either trialkylboranes or alkylboronic esters to produce alkylarylcarbinols in good yields after oxidation. This reaction provides a very facile procedure for the synthesis of alkylarylcarbinols.

## Introduction

The reactions of organoboranes with anions bearing leaving groups have been extensively studied and utilized in synthetic organic chemistry.<sup>1</sup> During the past decade, the reactions of organoboranes with  $\alpha$ -halomethyl anions<sup>2</sup> and  $\alpha,\alpha$ -dihalomethyl anions<sup>3</sup> have been used in natural product syntheses. Recently, Brown reported that the  $\alpha$ -chloroallyl anion, generated *in situ* from allyl chloride and lithium dialkylamide, would react with triisopropyl borate<sup>4a</sup> or 9-alkoxy-9-borabicyclo[3.3.1]nonane<sup>4b</sup> (9-alkoxy-9-BBN) to generate either the  $\alpha$ -chloroallylboronate ester or cyclooctane derivatives. We found that  $\alpha$ -chlorobenzyl anions could be generated from ( $\alpha,\alpha$ -dichloroaryl)methanes and that the resulting anions were captured *in situ* by trialkylboranes to afford alkylarylcarbinols after oxidation.<sup>5</sup> It is interesting to note that the reactions of trialkylboranes with other  $\alpha$ -substituted benzyl anions such as the  $\alpha$ -(phenylthio)benzyl anion, triphenylphosphonium benzylide, and triphenylarsonium benzylide were reported to produce alkylbenzenes and 1,2-diphenylalkanes.<sup>6</sup> We wish to report the results of a study in which ( $\alpha$ -chloroaryl)methyl anions, generated by deprotonation of arylmethyl chlorides with lithium dialkylamides at low temperature, react *in situ* with trialkylboranes or alkylboronic esters to give alkylarylcarbinols in very good yields after oxidation. The reaction pro-

vides a very facile synthesis of alkylarylcarbinols from arylmethyl chlorides and organoboranes.

## Results and Discussion

The reaction is initiated by the addition of a solution of lithium dialkylamide in THF to a mixture of an arylmethyl halide and an organoborane at low temperature. The mixture is stirred for 10 min and then warmed to 0 °C. Oxidation yields alkylarylcarbinols, as shown in Scheme 1.

The reaction of benzyl chloride with tributylborane was examined under a variety of conditions. The results of this study are summarized in Table 1.

As shown in Table 1, the reaction affords 1-phenyl-1-pentanol (**3a**) in high yields when it is carried out at low temperature (−78 °C) using a hindered base such as lithium dicyclohexylamide or lithium tetramethylpiperidide. Oxidation using either sodium perborate<sup>7</sup> or the modified hydrogen peroxide procedure<sup>4b</sup> generates the product in equivalent yields (Table 1, entries 4 and 6).

The reactions of various trialkylboranes with arylmethyl halides in the presence of lithium dicyclohexylamide, at −78 °C, were studied (Scheme 1). The results are outlined in Table 2.

As noted in Table 2, the alkylarylcarbinols are generally formed in very good yields when arylmethyl chlorides are utilized. The yields of carbinols decrease when arylmethyl bromides are used (Table 2, entries 10 and 11). This may be due to the more facile formation and greater stability of the ( $\alpha$ -chloroaryl)methyl anion compared to the ( $\alpha$ -bromoaryl)methyl anion.

The reaction presumably occurs via the intermediate formation of an ( $\alpha$ -haloaryl)methyl anion via the deprotonation of the arylmethyl halide with lithium dicyclohexylamide.<sup>8</sup> The  $\alpha$ -haloanion then reacts with trialkylboranes to form a borate complex that produces a new trialkylboranes via an anionotropic rearrangement, as outlined in Scheme 2.

(7) (a) Kabalka, G. W.; Shoup, T. M.; Goudgaon, N. M. *J. Org. Chem.* **1989**, *54*, 5930. (b) Matteson, D. S.; Moody, R. J. *J. Org. Chem.* **1980**, *45*, 1091.

(8) It has been reported that ( $\alpha$ -chlorobenzyl)lithium, generated *in situ* by the deprotonation of benzyl chloride with lithium diisopropylamide, reacts with trimethylsilyl chloride to produce  $\alpha$ -(trimethylsilyl)benzyl chloride in good yield but that 1-chloro-1,2-diphenylethane is formed in the absence of added electrophile. See: Andringa, H.; Heus-Kloos, Y. A.; Brandsma, L. *J. Organomet. Chem.* **1987**, *336*, C41.

\* Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic Press: London, 1988; pp 63–65, 261–273.

(2) (a) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687. (b) Sadhu, K. M.; Matteson, D. S. *Tetrahedron Lett.* **1986**, *27*, 795. (c) Brown, H. C.; Phadke, A. S.; Rangaishenvi, M. V. *J. Am. Chem. Soc.* **1988**, *110*, 6263. (d) Soundararajan, R.; Li, G.; Brown, H. C. *Tetrahedron Lett.* **1994**, *35*, 8957. (e) Soundararajan, R.; Li, G.; Brown, H. C. *Tetrahedron Lett.* **1994**, *35*, 8961.

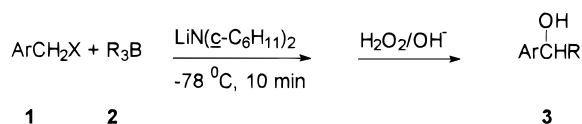
(3) (a) Matteson, D. S. *Acc. Chem. Res.* **1988**, *21*, 294 and references cited therein. (b) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535 and references cited therein. (c) Matteson, D. S.; Kandil, A. A.; Soundararajan, R. *J. Am. Chem. Soc.* **1990**, *112*, 3964. (d) Rangaishenvi, M. V.; Singaram, B.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 3286.

(4) (a) Brown, H. C.; Rangaishenvi, M. V. *Tetrahedron Lett.* **1990**, *31*, 7113. (b) Brown, H. C.; Jayaraman, S. *J. Org. Chem.* **1993**, *58*, 6791.

(5) (a) Kabalka, G. W.; Li, N.-S.; Yu, S. *Tetrahedron Lett.* **1995**, *36*, 8545. (b) Li, N.-S.; Yu, S.; Kabalka, G. W. *J. Organomet. Chem.*, in press.

(6) (a) Mukaiyama, T.; Yamamoto, S.; Shionon, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2244. (b) Koster, R.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 2782. (c) Tufariello, J. J.; Lee, L. T. C.; Wojtkowski, P. *J. Am. Chem. Soc.* **1967**, *89*, 6804.

Scheme 1



**Table 1. Preparation of 1-Phenyl-1-pentanol via the Reaction of Benzyl Chloride with Tributylborane under Various Reaction Conditions**

entry no.	base	reacn temp (°C)	oxidn reagent	yield <sup>a</sup> of <b>3a</b> (%)
1	LDA	0	NaBO <sub>3</sub> ·4H <sub>2</sub> O	30
2	LDA	-78	NaBO <sub>3</sub> ·4H <sub>2</sub> O	35
3	LiN(C-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> <sup>b</sup>	0	NaBO <sub>3</sub> ·4H <sub>2</sub> O	68
4	LiN(C-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> <sup>b</sup>	-78	NaBO <sub>3</sub> ·4H <sub>2</sub> O	86
5	LiTMP <sup>c</sup>	-78	NaBO <sub>3</sub> ·4H <sub>2</sub> O	87
6	LiN(C-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> <sup>b</sup>	-78	H <sub>2</sub> O <sub>2</sub> /OH <sup>-</sup>	86

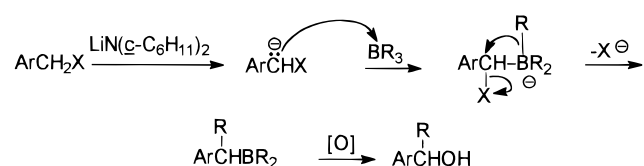
<sup>a</sup> Isolated yield of pure product. <sup>b</sup> Lithium dicyclohexylamide. <sup>c</sup> Lithium tetramethylpiperidide.

**Table 2. Alkylarylcarbinols Generated from the Reaction of Trialkylboranes with Arylmethyl Halides**

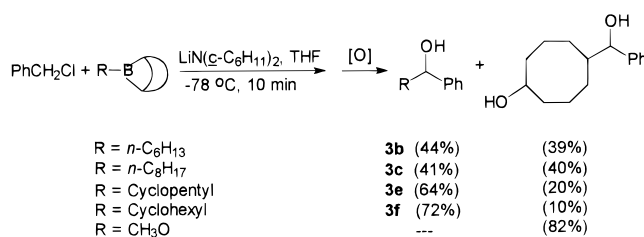
entry no.	product <sup>a</sup>	R	Ar	X	yield (%) <sup>b</sup>
1	<b>3a</b>	<i>n</i> -Bu	Ph	Cl	86
2	<b>3b</b>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Ph	Cl	91
3	<b>3c</b>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	Ph	Cl	76
4	<b>3d</b>	<i>sec</i> -Bu	Ph	Cl	76
5	<b>3e</b>	cyclopentyl	Ph	Cl	83
6	<b>3f</b>	cyclohexyl	Ph	Cl	83
7	<b>3g</b>	<i>n</i> -Bu	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Cl	82
8	<b>3h</b>	<i>n</i> -Bu	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Cl	82
9	<b>3i</b>	<i>n</i> -Bu	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Cl	86
10	<b>3a</b>	<i>n</i> -Bu	Ph	Br	62
11	<b>3j</b>	<i>n</i> -Bu	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	Br	61

<sup>a</sup> All reaction products exhibited physical and spectral characteristics in accord with literature values. <sup>b</sup> Isolated yields.

Scheme 2



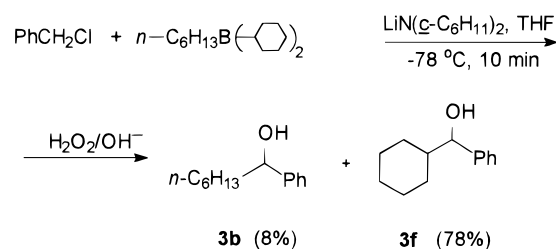
Scheme 3



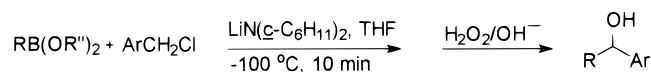
The disadvantage of using trialkylboranes is that only one alkyl group in the trialkylboranes is utilized; therefore, we investigated the use of borane derivatives such as 9-alkyl-9-BBN, alkyldicyclohexylborane, and alkylboronic ester reagents; the results are summarized in Schemes 3–5.

As shown in Scheme 3, 9-BBN derivatives readily react under the reaction conditions but the cyclooctyl group also migrates. In fact, 9-methoxy-9-BBN reacts with benzyl chloride in the presence of lithium dicyclohexylamide to give (5-hydroxycyclooctyl)phenylcarbinol

Scheme 4



Scheme 5



**Table 3. Alkylarylcarbinols from Alkylboronic Esters and Arylmethyl Chloride**

entry no.	product <sup>a</sup>	Ar	R	R'	temp (°C)	yield (%) <sup>b</sup>
1	<b>3a</b>	Ph	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	0	50
2	<b>3a</b>	Ph	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-78	78
3	<b>3a</b>	Ph	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-100	83
4 <sup>c</sup>	<b>3a</b>	Ph	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-100	43
5	<b>3b</b>	Ph	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	-100	82
6	<b>3k</b>	Ph	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	CH <sub>3</sub>	-100	80
7	<b>3c</b>	Ph	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	CH <sub>3</sub>	-100	76
8	<b>3e</b>	Ph	cyclopentyl	CH <sub>3</sub>	-100	86
9	<b>3g</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-100	73
10	<b>3h</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-100	76
11	<b>3i</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>n</i> -Bu	(CH <sub>3</sub> ) <sub>2</sub> CH	-100	78

<sup>a</sup> All reaction products exhibited physical and spectral characteristics in accordance with literature values. <sup>b</sup> Isolated yield. <sup>c</sup> LDA was used as a base in this experiment.

in very high yield (82%). The preference of the migration of the alkyl group in this reaction is cyclohexyl ≈ cyclopentyl > primary alkyl > cyclooctyl.

As noted in Scheme 4, dicyclohexylborane readily reacts with benzyl chloride in the presence of lithium dicyclohexylamide, followed by oxidation, to give carbinol **3b** in 8% yield and **3f** in 78% yield. These results suggest that the migration of the cyclohexyl group is 5 times faster than that of the *n*-hexyl group. Therefore, the utility of borane derivatives such as 9-alkyl-9-BBN and alkyldicyclohexylborane is limited due to the competitive migration of cyclooctyl and cyclohexyl groups.

The results of the reactions of various alkylboronic esters with arylmethyl chlorides in the presence of lithium dicyclohexylamide at -100 °C (Scheme 5) are summarized in Table 3. As noted, the reactions generally give alkylarylcarbinols in high yields (73–86%); the reactions are most efficient if lower temperatures and hindered bases are utilized.

It is interesting to note that, at -78 °C, butyldiisopropoxyborane affords 1-phenyl-1-pentanol (**3a**) in 78% yield, after oxidation; whereas *n*-butylcatecholborane yields only traces of **3a**, the major product being 1-chloro-1,2-diphenylethane.<sup>8</sup> Presumably, the catecholboronate ester is not sufficiently acidic to form the borate complex, which allows the coupling reaction to occur.

## Conclusion

The reaction described in this paper provides a useful, high-yield, one-pot synthesis of alkylarylcarbinols from organoboranes and arylmethyl chlorides. Both trial-

ylboranes and alkylboronic esters can be used as alkylating reagents.

### Experimental Section

All reagents and solvents were transferred using techniques designed to eliminate contact with air. All glassware and syringes were oven-dried for 24 h prior to use. THF was distilled from sodium benzophenone ketyl. Borane-THF complex (1.0 M solution in THF), *B*-Bromocatecholborane, *n*-butyllithium (1.6 M solution in hexane), 9-BBN, tributylborane (1.0 M solution in THF), tri-*sec*-butylborane (1.0 M solution in THF), 9-methoxy-9-BBN (1.0 M solution in hexane), and butyldiisopropoxyborane were purchased from Aldrich Chemical Co. and used as received. Alkenes and amines (Aldrich Chemical Co.) were dried by distillation from calcium hydride. Arylmethyl halides (Aldrich Chemical Co.) were distilled from phosphorus pentoxide prior to use. Trihexylborane, trioctylborane, tricyclopentylborane, and tricyclohexylborane were prepared by the hydroboration of alkenes with borane-THF complex.<sup>9</sup> 9-alkyl-9-BBN derivatives were prepared via the hydroboration of alkenes with 9-BBN.<sup>10</sup> *n*-Hexyldicyclohexylborane was prepared by the hydroboration of 1-hexene with dicyclohexylborane.<sup>11</sup> *n*-Butylcatecholborane was prepared via the reaction of *n*-butyllithium with *B*-bromocatecholborane in pentane at -78 °C. Other alkylboronic esters were prepared according to literature procedures.<sup>12</sup> Lithium dialkylamides were prepared *in situ* by metalating the corresponding amines in THF with *n*-BuLi at 0 °C and were used immediately. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using a Bruker AC-250 (250 MHz) NMR spectrometer.

The synthesis of 1-phenyl-1-pentanol (**3a**) (Table 3, entry 3) is representative: under an argon atmosphere, a solution of lithium dicyclohexylamide (2.5 mmol) in THF (2.5 mL) was added to a mixture of *n*-butyldiisopropoxyborane (2.5 mmol, 0.47 g) and benzyl chloride (2.5 mmol, 0.32 g) in THF (2.5 mL) at -100 °C (trialkylborane reactions can be carried out at -78 °C). After it was stirred at -100 °C for 10 min, the mixture was warmed to 0 °C and then oxidized using preformed peroxide anion generated by reacting 3 N NaOH (1.0 mL) with 30% H<sub>2</sub>O<sub>2</sub> (1.0 mL).<sup>4b</sup> The mixture was heated to 50 °C for 30 min to ensure completion of the oxidation and then cooled to room temperature. The product was extracted into ether (3 × 10 mL) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue purified by silica gel flash chromatography (eluent hexane/ethyl acetate, 9/1 (v/v)) to give 1-phenyl-1-pentanol (**3a**):<sup>5</sup> 0.34 g, 83% yield. A parallel reaction using tributylborane (2.5 mmol, 2.5 mL of a 1 M solution in THF) with benzyl chloride (2.5 mmol, 0.32 g) in the presence of lithium dicyclohexylamide (2.5 mmol) at -78 °C produced **3a** in 86% yield (Table 2, entry 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.29 (m, 5H), 4.60 (t, 1H, *J* = 6.7 Hz), 2.19 (br s, 1H), 1.88–1.56 (m, 2H), 1.45–1.12 (m, 4H), 0.87 (t, 3H, *J* = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 144.9, 128.3, 127.4, 125.9, 74.6, 38.8, 27.9, 22.6, 13.9 ppm.

All other alkylarylcarbinols were prepared via the procedure outlined for **3a**. Yields of the carbinols prepared from trialkylboranes or alkylboronic esters are indicated in Tables 2 and 3, respectively. The spectral characteristics of these compounds are as follows.

**1-Phenyl-1-heptanol (3b).**<sup>13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.28 (m, 5H), 4.56 (t, 1H, *J* = 6.6 Hz), 2.47 (br s, 1H), 1.84–

1.56 (m, 2H), 1.40–1.14 (m, 8H), 0.86 (t, 3H, *J* = 6.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 145.0, 128.2, 127.2, 125.8, 74.5, 39.0, 31.7, 29.1, 25.7, 22.5, 14.0 ppm.

**1-Phenyl-1-nonanol (3c).**<sup>14</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.28, (m, 5H), 4.57 (t, 1H, *J* = 6.6 Hz), 2.45 (br s, 1H), 1.87–1.55 (m, 2H), 1.48–1.22 (m, 12H), 0.87 (t, 1H, *J* = 6.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 145.0, 128.2, 127.2, 125.8, 74.5, 39.0, 31.8, 29.5, 29.5, 29.2, 25.7, 22.6, 14.0 ppm.

**1-Phenyl-2-methyl-1-butanol (3d).**<sup>15</sup> The ratio of the two diastereoisomers was 41:59, on the basis of <sup>1</sup>H NMR data.<sup>16</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS) δ 7.30 (m, 5H), 4.50 (d, 0.41 H, *J* = 5.9 Hz), 4.41 (d, 0.59H, *J* = 6.9 Hz), 2.00–1.84 (br s, 1H), 1.82–0.97 (m, 3H), 0.97–0.69 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.9, 143.6, 128.1, 128.0, 127.3, 127.2, 126.7, 126.3, 78.7, 78.0, 41.9, 41.6, 25.8, 24.8, 15.1, 13.9, 11.6, 11.3 ppm.

**Cyclopentylphenylmethanol (3e).**<sup>15</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.31 (m, 5H), 4.38 (d, 1H, *J* = 8.4 Hz), 2.29–2.10 (m, 1H), 1.99 (br s, 1H), 1.94–1.05 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 144.4, 128.3, 127.4, 126.5, 79.1, 47.6, 29.4, 29.3, 25.5, 25.4 ppm.<sup>17</sup>

**Cyclohexylphenylmethanol (3f).**<sup>15</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.29 (m, 5H), 4.35 (d, 1H, *J* = 7.1 Hz), 2.04–0.82 (overlapping signals, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.6, 128.1, 127.4, 126.6, 79.4, 44.9, 29.3, 28.8, 26.4, 26.1, 26.0 ppm.<sup>17</sup>

**1-(*p*-Methylphenyl)-1-pentanol (3g).**<sup>18</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.20 (d, 2H, *J* = 8.1 Hz), 7.12 (d, 2H, *J* = 8.1 Hz), 4.56 (t, 1H, *J* = 6.7 Hz), 2.32 (s, 3H), 2.24 (br s, 1H), 1.85–1.57 (m, 2H), 1.42–1.23 (m, 4H), 0.86 (t, 3H, *J* = 7.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 141.8, 136.9, 128.9, 125.8, 74.4, 38.6, 27.9, 22.5, 21.0, 13.9 ppm.

**1-(*p*-Methoxyphenyl)-1-pentanol (3h).**<sup>19</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.24 (d, 2H, *J* = 8.6 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 4.57 (t, 1H, *J* = 6.7 Hz), 3.78 (s, 3H), 2.23–2.04 (br s, 1H), 1.88–1.56 (m, 2H), 1.48–1.13 (m, 4H), 0.87 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 158.8, 137.1, 127.0, 113.6, 74.1, 55.1, 38.6, 28.0, 22.5, 13.9 ppm.

**1-(*p*-Chlorophenyl)-1-pentanol (3i).**<sup>20</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.29 (d, 2H, *J* = 8.5 Hz), 7.23 (d, 2H, *J* = 8.5 Hz), 4.58 (t, 1H, *J* = 6.6 Hz), 2.41–2.10 (br s, 1H), 1.83–1.54 (m, 2H), 1.43–1.14 (m, 4H), 0.87 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.3, 133.0, 128.4, 127.2, 73.9, 38.8, 27.8, 22.5, 13.9 ppm.

**1-(*p*-Bromophenyl)-1-pentanol (3j).**<sup>21</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.46, (d, 2H, *J* = 8.4 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 4.61 (t, 1H, *J* = 6.6 Hz), 2.02–1.92 (br s, 1H), 1.82–1.58 (m, 2H), 1.44–1.15 (m, 4H), 0.88 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.8, 131.3, 127.6, 121.0, 73.8, 38.7, 27.7, 22.5, 13.9 ppm.

**1-Phenyl-1-octanol (3k).**<sup>22</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 7.30 (m, 5H), 4.60 (t, 1H, *J* = 6.6), 2.21 (br s, 1H), 1.80–1.61 (m,

(14) Grundy, J. J. *Chem. Soc.* **1957**, 5087.

(15) Trahanovsky, W. S.; Fox, N. S. *J. Am. Chem. Soc.* **1974**, *96*, 7968.

(16) The modest diastereoselectivity apparently occurs due to energy differences arising from steric interactions present in the diastereomeric organoborate intermediates, i.e.



(17) The nonequivalence of the ring carbons in cycloalkyl groups attached to chiral centers has been noted previously. See for example: Pouchert, C. J.; Behnke, J. *The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1993; Vol. 2, spectrum 334B. Singleton, D. A.; Martinez, J. P.; Watson, J. V.; Ndip, G. M. *Tetrahedron* **1992**, *48*, 5831.

(18) Chibale, K.; Greeres, N.; Lyford, L.; Pease, J. E. *Tetrahedron: Asymmetry* **1993**, *4*, 2407.

(19) Palfray, L.; Metayer, M.; Panouse, J. *Bull. Soc. Chim. Fr.* **1947**, 766.

(20) Boots, M. R.; Boots, S. G.; Noble, C. M.; Guyer, K. E. *J. Pharm. Sci.* **1973**, *62*, 952.

(21) Brown, J. H.; Marvel, C. S. *J. Am. Chem. Soc.* **1937**, *59*, 1176.

(22) Jie, M. S. F. L. K.; Lam, W. L. K.; Lao, H. B. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1.

(9) Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

(10) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297.

(11) Brown, H. C.; Kabalka, G. W.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 4530.

(12) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.

(13) Gautier, J.-A.; Miocque, M.; Mascrier-Demagny, L. *Bull. Soc. Chim. Fr.* **1967**, 1554.

2H), 1.25 (br s, 10H), 0.87 (t, 3H,  $J = 7.0$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  144.9, 128.3, 127.3, 125.9, 74.6, 39.0, 31.8, 29.4, 29.2, 25.8, 22.6, 14.0 ppm.

**(5-Hydroxycyclooctyl)phenylcarbinol** was prepared by reacting 9-methoxy-9-BBN (2.5 mmol, 2.5 mL of 1 M solution in hexane) with benzyl chloride (2.5 mmol, 0.32 g) in the presence of lithium dicyclohexylamide (2.5 mmol) at  $-78$  °C. The product (0.48 g, 82% yield) was isolated by flash chromatography (eluent hexane/ethyl acetate, 2/8 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  7.31 (m, 5H), 4.40 (d, 1H,  $J = 6.8$ ), 4.00–3.85 (m, 1H), 2.02–1.14 (m, 15H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  143.7, 128.2, 127.4, 126.6, 79.4, 72.1, 44.2, 36.1, 36.0, 30.4, 28.5, 23.2,

22.8 ppm.<sup>17</sup> HRMS: calcd for  $\text{C}_{15}\text{H}_{20}\text{O}$  ( $\text{M} - \text{H}_2\text{O}$ ) 216.1514, found 216.1520.

9-Alkyl-9-BBN and *n*-hexyldicyclohexylborane were also reacted with benzyl chloride at  $-78$  °C. The yields of the corresponding alkylarylcarbinols are summarized in Schemes 3 and 4.

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