

# Regioselective cross-coupling of allylindium reagents with activated benzylic bromides—a simple and efficient procedure for the synthesis of terminal alkenes

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**Abstract**—Allylindium reagents undergo facile and highly regioselective cross-coupling with benzylic and cinnamyl bromides in THF at room temperature without any catalyst producing terminal alkenes in high yields. The addition is highly regioselective and is found to provide  $\gamma$ -adducts in all reactions.

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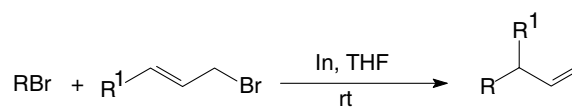
The allylation of an organic substrate is a very useful process as it provides a double bond, which can be further functionalized.<sup>1</sup> The most frequently used methods for allylation include addition of allylsilanes<sup>2</sup> or allylstannanes<sup>3</sup> to organic electrophiles catalyzed by Lewis acids. However, the difficulties associated with the preparation of regiochemically defined allylstannanes, their tendency to undergo allylic isomerization, removal of tin from the product, and finally the toxicity of tin, restrict the use of allylstannanes as nucleophilic coupling partners.<sup>3b</sup> Allylsilanes are also not very user-friendly being volatile. Allyl-magnesium and -lithium reagents are also used for allyl transfer to alkyl chains by halogen–metal exchange, however, these reagents show low functional group tolerance.<sup>4</sup>

Organoindium reagents are of considerable interest in organic synthesis because of their environmentally benign characteristics and their synthetic utility for carbon–carbon bond formation.<sup>5</sup> As part of our continued activities in the area of indium-mediated reactions<sup>6</sup> we are investigating novel applications of organoindium reagents in organic synthesis. Previously, we have described the indium mediated homocoupling of alkyl and aryl halides.<sup>6a</sup> Here, we demonstrate the regio-

selective cross-coupling of allylindium reagents with benzyl bromides leading to terminal alkenes (Scheme 1).

The experimental procedure is very simple.<sup>7</sup> A mixture of the benzyl bromide and allylindium reagent, prepared in situ from the reaction of indium metal and allyl bromide in THF, was stirred at room temperature until completion of the reaction (TLC). Workup and purification then provided the pure product. The products were characterized from their spectroscopic (IR, <sup>1</sup>H, and <sup>13</sup>C NMR) data.

Several substituted benzylic bromides underwent cross-coupling reactions with a variety of allylindium reagents at room temperature to produce the corresponding terminal alkenes, Table 1. As is evident from the results in Table 1,  $\gamma$ -addition products were obtained from the reactions of all the substituted allyl bromides (entries 3, 5, 6, 9, 10, 19, 20, and 22) although in principle, there was the possibility of formation of two products arising from  $\alpha$ - and  $\gamma$ -attack. The coupling reaction was found



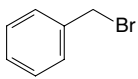
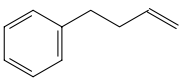
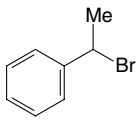
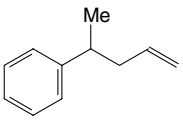
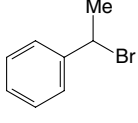
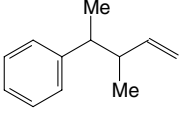
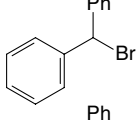
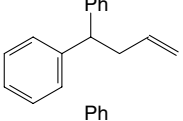
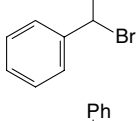
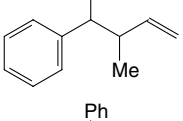
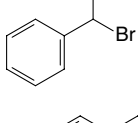
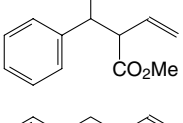
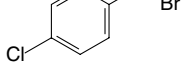
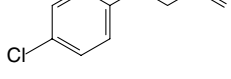
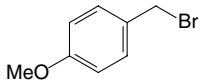
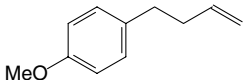
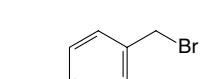
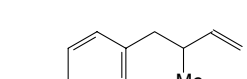
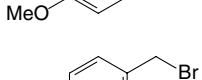
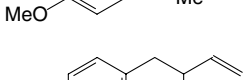
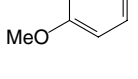
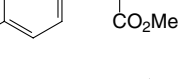
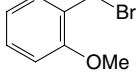
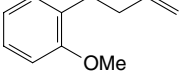
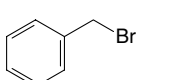
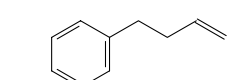
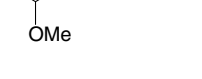
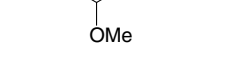
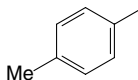
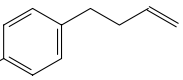
R = benzyl, R<sup>1</sup> = H, Me, CO<sub>2</sub>Me

Scheme 1.

**Keywords:** Indium metal; Allylation; Cross-coupling; Regioselectivity; Terminal alkenes.

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**Table 1.** Cross-coupling of organoindium reagents with benzyl bromides

Entry	RBr	R <sup>1</sup>	Product	Time (min)	Yield <sup>a</sup> (%)	Ref.
1		H		90	75	10
2		H		60	80	10
3		Me		60	70	11
4		H		20	90	10
5		Me		30	80	12
6		CO <sub>2</sub> Me		60	85	13
7		H		120	70	14
8		H		30	90	15
9		Me		45	80	16
10		CO <sub>2</sub> Me		30	90	—
11		H		40	85	19
12		H		85	78	20
13		H		45	85	19
14		H		240	30	21
15		H		240	37	—

(continued on next page)

Table 1 (continued)

Entry	RBr	R <sup>1</sup>	Product	Time (min)	Yield <sup>a</sup> (%)	Ref.
16		H		15	90	—
17		H		15	92	17
18		H		20	90	—
19		Me		35	80	—
20		CO <sub>2</sub> Me		60	85	—
21		H		30	86	—
22		Me		40	80	—
23		H		25	85	18
24		H		20	90	22

<sup>a</sup> Yields refer to those of pure isolated products fully characterized by spectroscopic data.

to be more facile when an electron donating group was present at the *para*-position of the aromatic ring of the benzylic bromides (entries 8–10, 13, and 16–22) compared to unsubstituted (entry 1) and more particularly, electron withdrawing group-substituted benzyl bromides (entries 7, 14, and 15). The *ortho*-electron donating substituted benzyl bromide (entry 11) also reacted in the same way as *p*-substituted examples. The reactions of *m*-methoxy-substituted benzyl bromide (entry 12) and cinnamyl bromide (entry 24) were comparable with their unsubstituted counterparts. However, aliphatic bromides remained virtually inert as was found by reaction with *n*-pentyl bromide; even after heating for 10 h at 70 °C, the reaction only proceeded marginally (10%). Both primary and secondary benzyl bro-

mides participated in this coupling reaction. Several functional groups present on the aromatic ring of the benzylic bromides, such as Cl, OMe, OBn, dioxymethylene, allyloxy, and propargyloxy remained unaffected under the reaction conditions.

In general, the reactions were very clean, fast, and high yielding. No Lewis acid catalysts, as usually employed for allylation reactions, were required in this procedure. The facile addition of  $\gamma$ -bromocrotonate to benzyl bromides provides an easy access to important substituted  $\beta,\gamma$ -unsaturated carboxylic esters (entries 6, 10, and 20). The highly selective  $\gamma$ -addition products provided by this reaction offer advantages over other existing procedures, which give mixtures of products.<sup>2–4</sup>

As is evident from the results, this cross-coupling reaction is very much influenced by the electronic effects of the substituents on the benzyl bromides. Thus, for a better understanding of the transition state, a Hammett correlation diagram has been drawn plotting  $\sigma$  (substituent constant) values of different substituents versus  $\log I$  ( $I$  = ratio of signal intensity of product with that of starting material after a certain period of time). The plot shows a negative slope ( $\rho$ ) of  $-1.956$  (Fig. 1), which indicates the involvement of a partial benzylic carbocation intermediate. As the  $\rho$  value of a typical  $S_N1$  reaction is approx.  $-4.5$ ,<sup>8</sup> here the reaction is neither a typical  $S_N1$  nor a classical  $S_N2$  process. Thus, a full positive charge at the benzylic carbon is unlikely for this reaction and a non-classical and non-concerted cyclic transition state (A) is thus postulated (Scheme 2), which favors  $\gamma$ -addition. This mechanism explains the facile reaction with an electron donating substituent, which stabilizes the benzylic carbocation favorably compared to an electron withdrawing group or with no substitution. This also gains support by the inertness of the alkyl bromide, which fails to provide sufficient stabilization of the carbocation to allow the reaction to progress.

In conclusion, the present procedure provides a novel protocol for the synthesis of terminal alkenes via highly

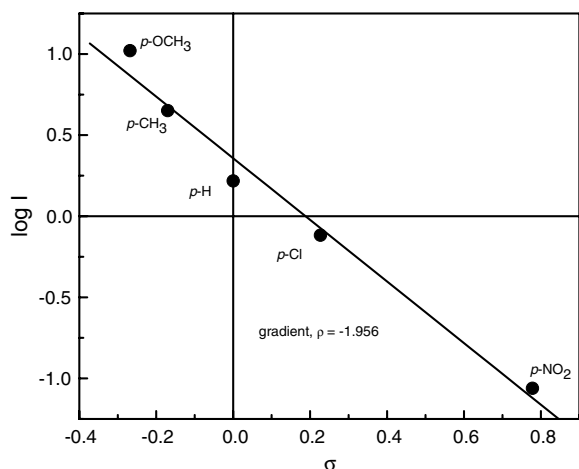


Figure 1. Hammett plot.

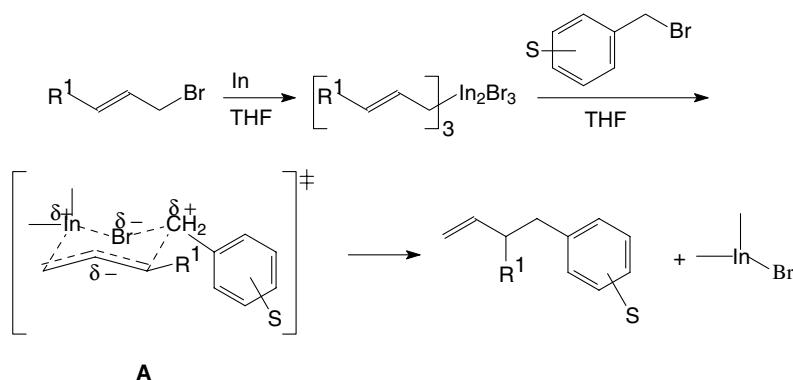
regioselective addition of benzyl bromides to allylindiums. We are not aware of any report addressing the catalyst-free cross-coupling of benzyl bromides and allylindiums, although similar Pd-catalyzed couplings of allylindiums with aryl halides have been reported.<sup>9</sup> Moreover, this procedure offers marked improvements with regard to operational simplicity, short reaction times, general applicability to substituted allylindiums, excellent regioselectivity, no requirement for a catalyst, and typically high isolated yields (75–95%). We believe, this reaction will find suitable applications in organic synthesis.

### Acknowledgments

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Scheme 2. A possible mechanism for the regioselective cross-coupling reaction of the organoindium reagent and benzyl bromides.

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7. **Representative procedure for coupling of allylindium with 4-methoxybenzyl bromide (Table 1, entry 8).** 4-Methoxybenzyl bromide (201 mg, 1 mmol) in THF (2 mL) was added to a well stirred mixture of allylindium reagent, prepared in situ by the reaction of indium metal (115 mg, 1 mmol) and allyl bromide (182 mg, 1.5 mmol) in THF (2 mL). The reaction mixture was stirred at room temperature for 30 minutes until completion of the reaction (TLC). The reaction mixture was quenched with brine, extracted with diethyl ether (3 × 10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave a crude residue, which was purified by short column chromatography over silica gel to provide a colorless liquid (147 mg, 90%), which was identified as 1-but-3-enyl-4-methoxybenzene by comparison of its spectroscopic data (IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR) with those reported.<sup>15</sup>
- This procedure was followed for the reactions listed in Table 1. The products (entries 1–9, 11–14, 17, 23, and 24) are known compounds and were identified by comparison of their spectroscopic data (IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR) with those reported (see references in Table 1). New compounds (entries 10, 15, 16, and 18–22) were characterized from their spectroscopic data and elemental analysis. These data are presented below:
- 2-(4-Methoxybenzyl)-but-3-enoic acid methyl ester (Table 1, entry 10):** Colorless liquid; IR (neat) 2958, 2934, 1736, 1514, 1248, 1167, 1034, 822 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.38–2.67 (m, 2H), 3.11–3.18 (m, 1H), 3.62 (s, 3H), 3.65 (s, 3H), 5.11–5.16 (m, 2H), 5.70–5.85 (m, 1H), 6.76–6.86 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 34.1, 48.6, 51.3, 51.9, 118.1, 122.9 (2C), 134.4 (2C), 134.5, 145.0, 166.4, 172.9. Anal. Calcd for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.89; H, 7.32. Found: C, 70.77; H, 7.25.
- 1-But-3-enyl-3-nitrobenzene (Table 1, entry 15):** Colorless liquid; IR (neat) 3026, 2976, 1639, 1599, 1493, 1450, 1032, 912, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.26–2.34 (m, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 4.93–5.04 (m, 2H), 5.77–5.85 (m, 1H), 7.49–7.60 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 5.5, 36.2, 115.4, 123.6, 124.3, 130.3, 135.4, 138.3, 140.1, 147.8 cm<sup>-1</sup>; Anal. Calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.62; H, 6.15; N, 7.78.
- 1-But-3-enyl-4-benzyloxybenzene (Table 1, entry 16):** Colorless liquid; IR (neat) 3030, 2962, 2916, 1510, 1454, 1242, 1026, 912, 734 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.37–2.45 (m, 2H), 2.72 (t, *J* = 7.78 Hz, 2H), 5.01–5.16 (m, 2H), 5.09 (s, 2H), 5.88–5.97 (m, 1H), 7.04 (d, *J* = 8.74 Hz, 2H), 7.24 (d, *J* = 8.73 Hz, 2H), 7.35–7.50 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 34.6, 35.8, 70.1, 114.8 (2C), 114.9, 127.6 (2C), 127.9, 128.6 (2C), 129.4 (2C), 134.3, 137.3, 138.3, 157.1. Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O: C, 85.67; H, 7.61. Found: C, 85.49; H, 7.51.
- 1-Allyloxy-4-but-3-enyl-benzene (Table 1, entry 18):** Colorless liquid; IR (neat) 2923, 2855, 1510, 1240, 997, 916, 825 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.35 (q, *J* = 7.59 Hz, 2H), 2.67 (t, *J* = 7.77 Hz, 2H), 4.53 (d, *J* = 5.23 Hz, 2H), 4.97–5.08 (m, 2H), 5.26–5.45 (m, 2H), 5.82–5.91 (m, 1H), 6.02–6.10 (m, 1H), 6.85 (d, *J* = 8.55 Hz, 2H), 7.11 (d, *J* = 8.49 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 34.6, 35.9, 68.9, 114.7 (2C), 114.9, 117.6, 129.4 (2C), 133.6, 134.3, 138.3, 156.9. Anal. Calcd for C<sub>13</sub>H<sub>16</sub>O: C, 82.94; H, 8.57. Found: C, 82.84; H, 8.43.
- 1-Allyloxy-4-(2-methyl-but-3-enyl)-benzene (Table 1, entry 19):** Colorless liquid; IR (neat) 3080, 2960, 2918, 2864, 1510, 1242, 1222, 1028, 997, 914, 833 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.78 (d, *J* = 6.42 Hz, 3H), 2.17–2.27 (m, 1H), 2.39–2.45 (m, 2H), 4.31 (d, *J* = 5.19 Hz, 2H), 4.70–4.77 (m, 2H), 5.05–5.24 (m, 2H), 5.53–5.62 (m, 1H), 5.81–5.88 (m, 1H), 6.63 (d, *J* = 8.48 Hz, 2H), 6.85 (d, *J* = 8.50 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 19.7, 39.8, 42.7, 69.3, 113.2, 114.8 (2C), 117.9, 130.5 (2C), 133.4, 133.9, 144.4, 157.2. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O: C, 83.12; H, 8.97. Found: C, 83.01; H, 8.85.
- 2-(4-Allyloxy-benzyl)-but-3-enoic acid methyl ester (Table 1, entry 20):** Colorless liquid; IR (neat) 2951, 2924, 2856, 1736, 1510, 1242, 1176, 1026, 997, 924 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.75–3.06 (m, 2H), 3.25–3.36 (m, 1H), 3.63 (s, 3H), 4.50 (d, *J* = 5.26 Hz, 2H), 5.05–5.13 (m, 2H), 5.25–5.43 (m, 2H), 5.79–5.87 (m, 1H), 6.00–6.06 (m, 1H), 6.82 (d, *J* = 8.51 Hz, 2H), 7.06 (d, *J* = 8.50 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 37.7, 51.9, 52.4, 68.9, 114.7 (2C), 117.6, 117.7, 130.1 (2C), 130.9, 133.5, 135.5, 157.3, 173.9. Anal. Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C, 73.15; H, 7.37%. Found: C, 73.01; H, 7.25.
- 1-But-3-enyl-4-prop-2-ynyloxybenzene (Table 1, entry 21):** Colorless liquid; IR (neat) 3294, 3074, 2924, 2856, 1639, 1610, 1510, 1298, 1263, 1219, 1031, 914, 825 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.39 (q, *J* = 7.37 Hz, 2H), 2.54 (t, *J* = 2.23 Hz, 1H), 2.70 (t, *J* = 6.40 Hz, 2H), 4.69 (d, *J* = 2.23 Hz, 2H), 5.01–5.23 (m, 2H), 5.85–5.95 (m, 1H), 6.95 (d, *J* = 8.52 Hz, 2H), 7.16 (d, *J* = 8.48 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 34.6, 35.8, 55.9, 75.4, 78.9, 114.9 (2C), 115.0, 129.3 (2C), 134.9, 138.2, 155.8. Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O: C, 83.83; H, 7.58. Found: C, 83.70; H, 7.41.
- 1-(2-Methyl-but-3-enyl)-4-prop-2-ynyloxybenzene (Table 1, entry 22):** Colorless liquid; IR (neat) 3296, 2963, 2920, 2864, 1610, 1510, 1217, 1032, 916, 835, 673 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.00 (d, *J* = 6.31 Hz, 3H), 2.38–2.46 (m, 1H), 2.51 (d, *J* = 7.00 Hz, 2H), 2.64 (t, *J* = 6.28 Hz, 1H), 4.68 (d, *J* = 2.15 Hz, 2H), 4.93–4.99 (m, 2H), 5.76–5.87 (m, 1H), 6.91 (d, *J* = 8.45 Hz, 2H), 7.10 (d, *J* = 8.48 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 19.7, 39.8, 42.7, 56.6, 75.7, 79.2, 113.2, 114.9 (2C), 130.5 (2C), 134.2, 144.4, 156.2. Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O: C, 83.96; H, 8.05. Found: C, 83.79; H, 7.92.
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