

## Cobalt(I) Catalyzed Reaction of Benzaldehydes with Functionalized Benzylic Zinc Halides

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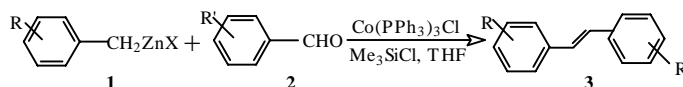
**Abstract:** Functionalized benzylic zinc halides reacted with benzaldehydes in the presence of Lewis acid  $\text{Me}_3\text{SiCl}$  giving high yields of *trans*-stilbenes under the catalysis of  $\text{Co}(\text{PPh}_3)_3\text{Cl}$ .

**Keywords:** Co(I) catalysis, functionalized benzylic zinc halides, benzaldehydes, stilbenes.

Organozincs are an important class of organometallics for organic and organometallic synthesis<sup>1</sup>. But direct addition of organic zinc halides to aldehydes is usually inefficient<sup>2</sup>. However, it was found that these reactions can be carried out efficiently in the presence of Lewis acid such as  $\text{BF}_3\cdot\text{OEt}_2$ <sup>3</sup> by transmetallized these reagents to corresponding copper compounds. When the organic moieties in organozincs were benzylic groups, transmetallation to corresponding copper reagents was found to be a mandatory procedure and 1, 2-diarylethanols were obtained in excellent yields<sup>4</sup>.

Owing to our interest in the reaction of organozincs with aldehydes<sup>5</sup>. We used substituted benzylic zinc reagents in our experiments. Amazingly, we found that *trans*-stilbenes can be obtained from benzylic zinc halides with benzaldehydes in the presence of catalytic amount of  $\text{Co}(\text{PPh}_3)_3\text{Cl}$  using a silylating agent (**Scheme 1**).

Scheme 1



$\text{Me}_3\text{SiCl}$  plays a major role in these reactions. Without  $\text{Me}_3\text{SiCl}$ , benzylic zinc halides did not react with benzaldehydes at all. The catalyst  $\text{Co}(\text{PPh}_3)_3\text{Cl}$  is also necessary for this reaction. In case of absence of the cobalt complex, the yield of *trans*-stilbene would be low.

The substituent effect was also studied in these reactions. Electron donating groups on both benzene rings of benzaldehydes and benzylic halides can accelerated these reactions. The yield of stilbenes is also high. Whereas a nitro functionality in benzylic halide completely inhibits zinc insertion. Benzaldehydes with nitro substituent were also found to be inert to this kind of organometallics.

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Benzylic zinc halides (6 mmol) were prepared as Berk procedure<sup>4</sup>.  $\text{Co}(\text{PPh}_3)_3\text{Cl}$  (0.27 g, 0.3 mmol) dissolved in THF (2 mL) was added to a solution of benzylic zinc halides at 0°C. After 2 min stirring, the mixture was cooled to -18°C and a solution of benzaldehyde (5 mmol),  $\text{Me}_3\text{SiCl}$  (1.9 g, 10 mmol) in THF (10 mL) was then added dropwise. The reaction mixture was stirred for 12 h and the reaction temperature was allowed to rise to room temperature. After usual workup, *trans*-stilbenes<sup>6</sup> were obtained by chromatography on a silica gel using petroleum ether/ethyl acetate as an eluent (Table 1).

**Table 1** The yield and mp of the *trans*-Stilbenes<sup>a</sup>

<b>3</b>	R	X	R <sup>1</sup>	Yield/%	Mp (lit)/°C
<b>a</b>	H	Cl	H	86	125-127 (124-125 <sup>7</sup> )
<b>b</b>	H	Cl	4-OMe	88	138-139 (135-136 <sup>7</sup> )
<b>c</b>	H	Cl	2-OMe	81	58-59 (58.6-59.5 <sup>7</sup> )
<b>d</b>	H	Cl	4-OH	82	188-189 (192-193 <sup>8</sup> )
<b>e</b>	H	Cl	2-OH	74	145-146 (143-144 <sup>9</sup> )
<b>f</b>	H	Cl	4-Cl	86	129-129.5 (129.2-129.6 <sup>7</sup> )
<b>g</b>	3-Cl	Br	H	78	73-74 (73-74 <sup>8</sup> )
<b>h</b>	4-Cl	Br	H	85	129-129.5 (129.2-129.6 <sup>7</sup> )
<b>i</b>	3-Br	Br	H	77	89-90 (89-90 <sup>10</sup> )
<b>j</b>	4-Br	Br	H	83	136-137 (136-137.6 <sup>7</sup> )

a: All the products are well known compounds and were characterized by IR, <sup>1</sup>H NMR and MS.

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### References and Notes

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- Spectra data for **3c**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ ppm) 7.62-7.50 (m, 4H, Ar-H), 7.39-7.19 (m, 4H, Ar-H), 7.10, (d, 1H, *J*=16.6 Hz, =CH), 6.94 (dd, 2H, *J*<sub>1</sub>=18.6Hz, *J*<sub>2</sub>=7.0 Hz, =CH, ArH), 3.88 (s, 3H, OCH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): ν 3017, 2969, 2841, 1600, 1591, 1569, 1483, 1466, 1241, 1030, 965, 753, 691. EI-MS (*m/z*): 210 (100, M<sup>+</sup>), 195 (4, M<sup>+</sup>-CH<sub>3</sub>), 179 (13, M<sup>+</sup>-OCH<sub>3</sub>), 165 (40, M<sup>+</sup>-OCH<sub>3</sub>-CH<sub>2</sub>), 152 (12, M<sup>+</sup>-OCH<sub>3</sub>-C<sub>2</sub>H<sub>3</sub>), 139 (4, M<sup>+</sup>-OCH<sub>3</sub>-C<sub>3</sub>H<sub>4</sub>), 128 (2, M<sup>+</sup>-OCH<sub>3</sub>-C<sub>4</sub>H<sub>3</sub>), 115 (3, M<sup>+</sup>-OCH<sub>3</sub>-C<sub>5</sub>H<sub>4</sub>), 104 (17, M<sup>+</sup>-OCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>), 91 (24, C<sub>6</sub>H<sub>5</sub>CH<sup>+</sup>+1), 77 (3, C<sub>6</sub>H<sub>5</sub><sup>+</sup>).
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