

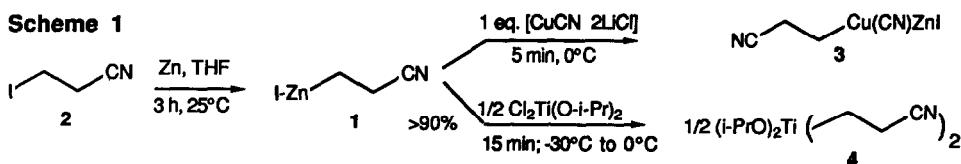
## 2-Cyanoethylzinc Iodide: A New Reagent with Reactivity Umpolung

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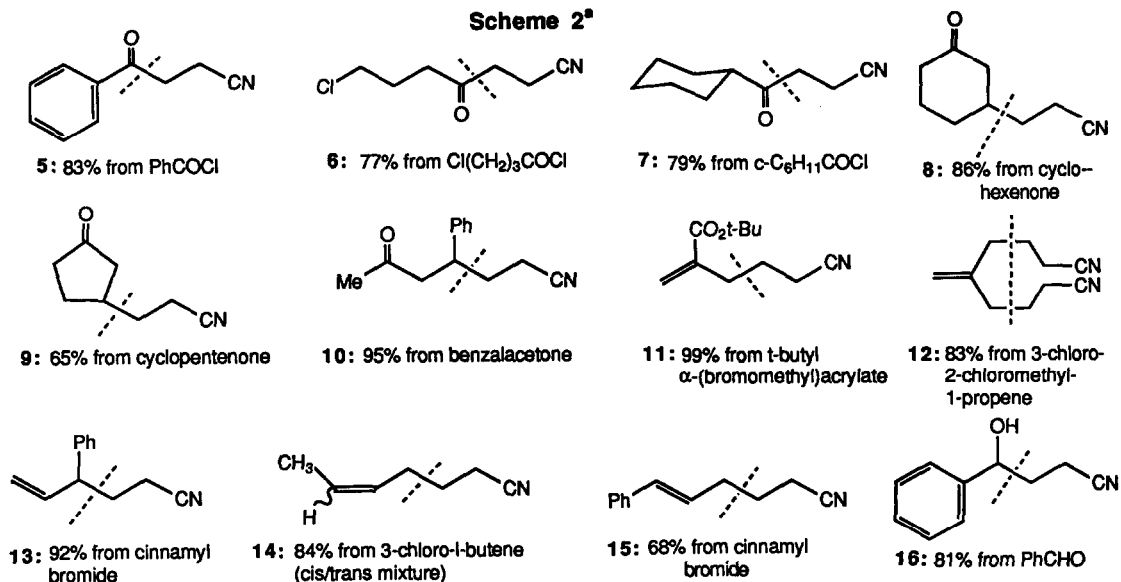
**Summary:** 2-Cyanoethylzinc iodide **1** generated in over 90% yield from 3-iodopropionitrile and zinc in THF can be transmetallated to the copper and titanium derivatives **3** and **4** which react in good yields, respectively, with acyl chlorides, enones, allylic halides and benzaldehyde.

Several functionalized zinc organometallics containing a halide,<sup>1</sup> an ester,<sup>2,3</sup> a cyano<sup>-3</sup> or even a ketone<sup>-3,4</sup> group have been reported and used to form new carbon-carbon bonds. We have recently found that various polyfunctional alkyl iodides can be converted into the corresponding zinc derivatives in high yields<sup>3</sup> by using zinc (activated with 4% of 1,3-dibromoethane and 3% chlorotrimethylsilane) in THF under very mild conditions (25°C for secondary iodides, 25-40°C for primary iodides). These zinc iodides could be transmetallated into copper compounds of the new<sup>3</sup> type RCu(CN)ZnI by using the soluble copper salt CuCN·2LiX (X = Br, Cl). We now report that our method allows the generation of 2-cyanoethylzinc iodide **1** from 3-iodopropionitrile **2** and zinc in THF at 25°C in over 90% yield. Compound **1** could then be transmetallated<sup>3</sup> with CuCN·2LiCl and Cl<sub>2</sub>Ti(O*i*-Pr)<sub>2</sub><sup>6</sup> into the copper and titanium organometallics tentatively represented by **3** and **4**, respectively (see Scheme 1). These new d<sup>3</sup>-reagents<sup>7</sup>



react readily with various organic electrophiles. Thus, the addition of acyl chlorides (0.8 eq.; 0°C; 2 h) to the copper compound **3** afforded the β-cyano ketones **5-7** in 77-83% yield (see Scheme 2). By the reaction of **3** with enones (0.8 eq.; -78°C to 25°C) in the presence of chlorotrimethylsilane<sup>8</sup> (2 eq.), the 1,4-addition products **8-10** are obtained in satisfactory yields (65-95%; see Scheme 2). Allylic halides (0.8 eq.) react with **3** and furnish the allylated products **11-14** (0°C; 2.5 h; 83-99%). This reaction proceeds regiospecifically<sup>9</sup> and cinnamyl bromide and 3-chloro-1-butene afford only the S<sub>N</sub>2' products **13** and **14**. The S<sub>N</sub>2 substitution product **15** can also be obtained regiospecifically by directly treating the zinc reagent **1** with cinnamyl bromide (0.8 eq.) in the presence of 1 mol % of Pd(PPh<sub>3</sub>)<sub>4</sub> (12 h; 45°C; 68%). Finally, while reaction of **1** with aldehydes is very sluggish, the titanium reagent **4** (1.5 eq.) reacts with benzaldehyde to furnish the addition product **16** (0°C, 3 h; 25°C, 3 h; 81%).

Further synthetic applications of substituted derivatives of **1** as well as the determination of the X-ray structure of **1** are currently underway in our laboratory.

Scheme 2<sup>a</sup>

<sup>a</sup>All indicated yields are isolated yields. Satisfactory spectral data (IR, <sup>1</sup>H and <sup>13</sup>C-NMR, mass spectra) and elemental analysis were obtained for all new compounds. The newly formed bonds are indicated by dotted lines.

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