

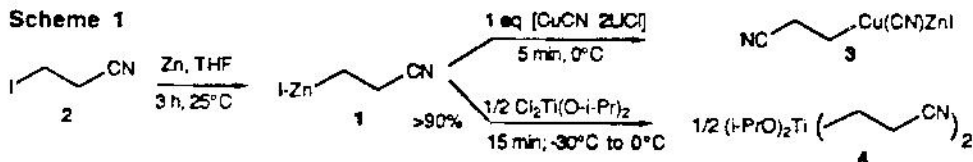
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Summary: 2-Cyanoethylzinc iodide **1** generated in over 90% yield from 3-iodopropionitrile and zinc in THF can be transmetalated to the copper and titanium derivatives **3** and **4** which react in good yields, respectively, with acyl chlorides,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

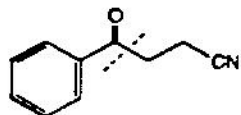
Several functionalized zinc organometallics containing a halide,¹ an ester,^{2,3} a cyano³ or even a ketone^{3,4} group have been reported and used to form new carbon-carbon bonds. We have recently found that various polyfunctional alkyl iodides can be converted into the corresponding zinc derivatives in high yields³ 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 transmetalated into copper compounds of the new³ type $\text{RCu}(\text{CN})\text{ZnI}$ by using the soluble copper salt $\text{CuCN}\cdot 2\text{LiX}$ ($\text{X} = \text{Br}, \text{Cl}$). We now report that our method allows the generation of 2-cyanoethylzinc iodide **1** from 3-iodopropionitrile **2**⁵ and zinc in THF at 25°C in over 90% yield. Compound **1** could then be transmetalated³ with $\text{CuCN}\cdot 2\text{LiCl}$ and $\text{Cl}_2\text{Ti}(\text{O}-i\text{-Pr})_2$ ⁶ into the copper and titanium organometallics tentatively represented by **3** and **4**, respectively (see Scheme 1). These new d^3 -reagents⁷

Scheme 1

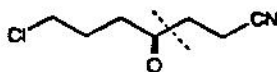
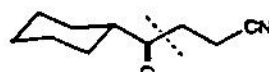
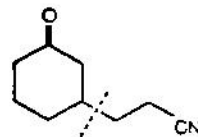


react readily with various organic electrophiles. Thus, the addition of acyl chlorides (0.8 eq.; 0°C; 2 h) to the copper compound **3** afforded the β -cyano ketones **5-7** in 77-83% yield (see Scheme 2). By the reaction of **3** with enones (0.8 eq.; -78°C to 25°C) in the presence of chlorotrimethylsilane⁸ (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 regiospecifically⁹ and cinnamyl bromide and 3-chloro-1-butene afford only the $\text{S}_{\text{N}}2'$ products **13** and **14**. The $\text{S}_{\text{N}}2$ 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 $\text{Pd}(\text{PPh}_3)_4$ (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%).

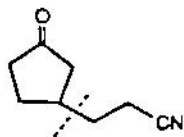
Further synthetic applications of substituted derivatives of **1** as well as the determination of the X-ray structure of **1** are currently underway in our laboratory.

Scheme 2^a

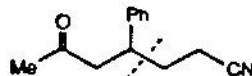
5: 83% from PhCOCl

6: 77% from Cl(CH₂)₃COCl7: 79% from *o*-C₆H₁₁COCl

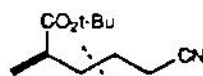
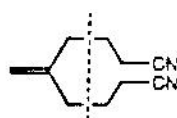
8: 86% from cyclohexenone



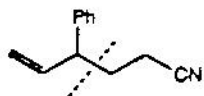
9: 65% from cyclopentenone



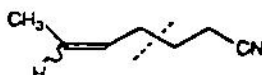
10: 95% from benzalacetone

11: 99% from *t*-butyl α -(bromomethyl)acrylate

12: 83% from 3-chloro-2-chloromethyl-1-propene



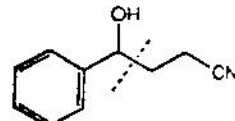
13: 82% from cinnamyl bromide



14: 84% from 3-chloro-1-butene (cis/trans mixture)



15: 68% from cinnamyl bromide



16: 81% from PhCHO

^aAll indicated yields are isolated yields. Satisfactory spectral data (IR, ¹H and ¹³C-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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