Unsymmetrical Cyano-cuprates as Reagents in Substitution and Addition Reactions

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Summary Unsymmetrical cyano-cuprates prepared by treating CuCN with RLi, can be used instead of R_2CuLi in substitution and addition reactions.

IN a recent paper Corey and Beames[1] showed that unsymmetrical lithium cuprate complexes, such as $[R^2\text{–C}\equiv\text{C–Cu–}R^1]^-Li^+$, react with cyclohexenone by transferring R^1 (alkyl or alkenyl) to the β position of the enone system, to give the β substituted cyclohexanone. This reaction is useful because it requires only 1 equiv. of R^1Li to form the alkylating reagent.

For some time[2] we have been attempting to develop an analogous reagent and report here that unsymmetrical lithium cuprate complexes, presumably $[N\equiv\text{C–Cu–R}]^-Li^+$, can be made simply by treating CuCN with alkyl-lithium (1 equiv.), and can be used instead of the symmetrical complexes R_2CuLi. These complexes are useful in performing 1,4 additions with unsaturated ketones, and in displacing halide ions from alkyl halides, the yields being in some instances better than those obtained with the symmetrical complexes. Some examples are reported in the Table.

These results are reminiscent of the reports by House and Fischer,[3] and by Normant, Bourgain, and Rone,[4] that sodium and lithium cyanides are useful for improving the reaction conditions of the substitution of aryl and vinyl halides by CuCN[3] and of allyl halides by copper(I) acetylides.[4] Presumably, in these cases, as well as in those reported here, symmetrical $[Cu(CN)_2Na]$ and unsymmetrical (RCuCNLi) cyano-cuprates are involved.

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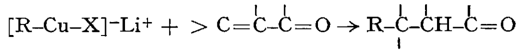
TABLE

Substitution

$$[R^1\text{–Cu–X}]^-Li^+ + R^2Br \rightarrow R^1\text{–}R^2 + CuX + LiBr$$

				Yield (%)	
R^1	X	R^2	Cu^I : halide	R^1–R^2	R^1–H[e]
Me	Me	1-Adamantyl[a]	4	80	
,,	CN	,, [a]	,,	35	
,,	Me	*endo*-3-Bornyl-2-oxo[b]	2·5	4	96
,,	CN	,, [b]	,,	21	72

Addition



$$[\text{R–Cu–X}]^-Li^+ + \,>C{=}\overset{|}{C}\text{–}\overset{|}{C}{=}O \rightarrow \text{R–}\underset{|}{\overset{|}{C}}\text{–CH–}\overset{|}{C}{=}O$$

R	X	Enone	Cu^I : enone	Yield (%)
Me	Me	Cyclohexenone[c]	1 : 1	97
,,	,,	,, [c]	7·3 : 1	91
Me	CN	,, [c]	1 : 1	44
,,	,,	,, [c]	7·3 : 1	88
Bu	Bu	,,	1 : 1	91
,,	,,	,,	7·3 : 1	100
Bu	CN	,,	1 : 1	51
,,	,,	,,	7·3 : 1	96
Me	Me	Benzylidene-acetone[d]	1 : 1	84
Me	CN	,,	,,	53
Ph	Ph	,,	,,	54
Ph	CN	,,	,,	25

[a] Time of reaction 96 h, at 35°. [b] 1 h at 0°. [c] 5 min at −59° [d] 5·5 h at 0°. [e] After hydrolysis.

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[4] J. Normant, M. Bourgain, and A. M. Rone, *Compt. rend.*, 1970, **270C**, 354; M. Bourgain, Ph.D. Thesis, University of Paris, 1972.