Lithium Diethylcuprate–
Triethylphosphine

(Et₂CuLi)

[38297-20-0] C₄H₁₂CuLi (MW 202.36)

InChIKey = TUQOTMZNTHZOKS-UHFFFAOY AQ

C₁₂H₂₇P (MW 202.36) [998-40-3] InChIKey = NPOGNLMQFUQKBZ-RHJPCPLGAO

(Bu₃P)

[998-40-3] C₁₅H₂₇P (MW 202.36)

InChIKey = TUQOTMZNTHZOKS-UHFFFAOY AQ

(representative phosphine-ligated homocuprate for 1,4-addition, nucleophilic substitution, and reductive metalation)

Solubility: sol ether, THF.

Analysis of Reagent Purity: an assay to determine relative thermal stabilities can be used to estimate reaction quality and concentration: a sample of known volume and temperature is quenched with excess PhCOCl. The yield of propiophenone is measured by GC, the response of which is calibrated using authentic product and n-dodecane as internal standard.

Preparative Methods: the following general procedure has been used to prepare a variety of R₂CuLi-P(n-Bu)₃ reagents: a round-bottom flask equipped with magnetic stirring bar and rubber septum is charged with authentic product and is measured by GC, the response of which is calibrated using adequate product and n-dodecane as internal standard.

Handling, Storage, and Precautions: best results are obtained with high purity Cu salts, dry, O₂-free solvents, and alkyl lithium solutions free of contaminating alkoxides or hydroxides. Like most alkyl lithium reagents, Ethylolithium is pyrophoric, care must be exercised in its handling. Homocuprates are stabilized in the presence of stoichiometric quantities of (n-Bu)₃P, there is no noticeable decomposition at −78°C. Use in a fume hood.

General Discussion. Phosphine-ligated homocuprates were introduced early in the development of organocopper chemistry. The (n-Bu)₃P ligand solubilizes the homocuprate in ether solvents, increasing its reactivity, and also retards thermal decomposition. Generally, the presence of stoichiometric quantities of the ligand makes reaction workup unsatisfactory, for this reason, various heterocuprates have found wider application in organic chemistry. Eq 1 provides a typical comparison.

\[
\text{X} \text{t-BuCul} + \text{C}_4\text{H}_9\text{Br} \xrightarrow{\text{THF}} \text{t-BuC}_3\text{H}_2\text{I} \quad (1)
\]

Lithium diethylcuprate–tributylphosphine has been essentially unused in organic synthesis. Phosphine-ligated organocopper reagents, however, have found recent applications in tandem vicinal dialkylation reactions leading to prostaglandins. Other reports suggest that the presence of a phosphine ligand during organocopper-mediated epoxide openings is important in promoting reductive metalation of substrate.

Related Reagents. Lithium Diethylcuprate; Lithium Dimethylcuprate; Lithium Divinylcuprate–Triethylphosphine.

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