Subtle factors are important: radical formation and transmetallation in reactions of butyl cuprates with cyclohexyl iodide.
(Electronic Supplementary Information)

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Experimental Section

New borosilicate vials (15 mL, Kimax®) were used as 'virgin' glassware. The 25-mL round-bottom flasks used as 'etched' glassware were borosilicate glass (Kimax®); they were >1 year old and had been used for many kinds of laboratory operations, including those that involved scraping with a metal spatula. They were routinely cleaned in a base bath (KOH/isopropyl alcohol), followed by aqueous Alconox® and deionized water. Thus, they had become mechanically and chemically etched. All glassware was rinsed with acetone and dried in an oven at 180 °C for at least 10 h before use.

The polypropylene test tubes (Fisher #14-956-1G) were sealed with rubber septa (Aldrich #Z10,074-9) and contained Teflon®-coated magnetic stirbars (Fisher #14-511-60B), which mixed the contents efficiently, as they rotated rapidly about the vertical axis of the tube.

'Ultrapure' CuI was nominally 99.999% pure (Aldrich #21,555-4, lots 12202 JU, 06303 PS and 08502 BQ). CuCN was nominally 99% pure (Aldrich #21,630-5, lot 07824 PS). Cyclohexyl iodide (Aldrich #23,824-4, 98%) was distilled under aspirator vacuum and then passed through a column of basic alumina (activity I) to make sure it was dry. BuLi (ca. 2.5 M) was supplied by FMC Corporation; it was standardized by using the Gilman double titration. When the residual base reached 20% of the active reagent, it was discarded.

Dry THF was provided by continuous stills, containing either Na and benzophenone or K metal.

In a typical blank reaction 1.00 mmol of BuLi (e.g., 0.45 mL of a 2.23-M solution) was added via gas-tight syringe to 7.0 mL of dry THF, containing 100 μL (73.0 mg) of decane at –78 ºC under Ar, and the mixture was immediately quenched with 3 mL of 3-M aqueous ammonium chloride, which had been deoxygenated by sparging with Ar. The amounts of BuBu, measured by GLC, ranged from 1.32-2.07% / mmol BuLi.

In a typical control reaction, a 2.00-mmol aliquot of BuLi was added to 1.00 mmol of CuI (190.4 mg) or CuCN (89.6 mg) in 7.0 mL of dry THF containing 100 μL (73.0 mg) of decane at –78 ºC under Ar. The reaction mixture was annealed at 0 ºC for 0.1 h and then cooled to –78 ºC, where it was quenched with 3 mL of Ar-sparged 3-M aqueous ammonium chloride. The amounts of BuBu, measured by GLC, were 12.3±1.9% / mmol Bu$_2$CuLi·LiI and 4.5±0.3% / mmol Bu$_2$CuLi·LiCN. Corrected for the corresponding blanks, the amounts of BuBu generated during cuprate preparation were 9.6% and 0.9%, which we have rounded to 10% and 1% per mmol of cuprate, respectively.

For reactions with CyI, a portion of CuI (191.0±0.2 mg) or CuCN (90.0±0.2 mg) was weighed into a dry reaction vessel and a magnetic stirbar was inserted. The vessel was carefully purged with Ar for 3 min and sealed with a rubber septum. Internal standard (100 μL, 73.0 mg, of decane) was added via syringe. Dry THF was added via syrine, rinsing down the walls of the vessel as much as possible to ensure that all of the Cu(I) salt was suspended. The amount of THF was chosen so that the final concentration of the reaction mixture was 0.125, 0.25 or 0.50 M. A positive pressure of Ar was maintained via a needle attached to a cut-off 1-mL syringe barrel, which was connected to a manifold with rubber tubing.

The reaction vessel was cooled to –78 ºC for 0.1 h with stirring, and 2.00 mmol of BuLi was added. The suspension was stirred at –78 ºC for 0.1 h and then annealed at 0 ºC for 0.1 h. The resulting black solution of **1a** or light yellow solution of **1b** was cooled to –78 ºC for 0.1 h, and 130.0 μL (1.01 mmol) of cyclohexyl iodide was added via gas-tight syringe. After the reaction time had elapsed, 3 mL of Ar-sparged 3-M aqueous ammonium chloride was added, and the reaction vessel was immediately removed from the cold bath (dry ice/acetone-isopropyl alcohol) and warmed by hand until all the ice inside had melted. The organic layer was separated, diluted with an equal volume of ether, and dried over anhydrous sodium sulfate.

GLC analyses were run in split mode (200:1) with an HP 6890 gas chromatograph equipped with a 30-m HP-1 capillary column (0.32 mm id, 0.25 μm film) and FID. It was calibrated before, during, and after each series of samples with a standard solution containing known amounts of authentic products and decane, e.g., (in order of elution) 774.4 mg of CyH, 408.9 mg of Cy(–H), 350.3 mg of BuBu, 368.6 mg of decane, 404.4 mg of BuCy, 411.2 mg of CyI and 450.5 mg of CyCy in 100 mL of ether. Area counts for a typical injection (1 μL) of this standard were 10983, 5867, 6687, 5115, 5732, 2299 and 6361, respectively.

Table 2 Yields and conversions (%) of products after 4 s from butyl cuprates and cyclohexyl iodide in polypropylene (K still).[a]

entry	reagent	*c* (M)	time (h)	BuCy	CyH	Cy(–H)	CyCy	BuBu[b]	C_{Bu}	C_{Cy}
1	Bu$_2$CuLi·LiI	0.12	0.001	16.9	1.1	1.0	1.6	<1	8.4	20.6
2		0.12	0.001	15.4	8.5	1.6	2.6	2.2	9.9	28.1
3		0.12	0.001	14.3	3.5	1.2	1.9	<1	7.1	20.9
4		0.12	0.001	20.6	1.1	0.9	1.3	<1	10.3	23.9
5		0.12	0.001	22.5	3.0	1.6	2.4	<1	11.2	29.5
6	Bu$_2$CuLi·LiCN	0.12	0.001	2.3	<0.1	<0.1	<0.1	<1	1.1	2.3
7		0.12	0.001	1.9	1.1	0.2	1.5	<1	0.9	4.7
8		0.12	0.001	2.0	<0.1	<0.1	<0.1	<1	1.0	2.0
9		0.12	0.001	2.5	<0.1	<0.1	<0.1	<1	1.2	2.5
10		0.12	0.001	0.6	0.3	<0.1	0.1	<1	0.3	1.0

[a] Determined by GLC calibrated with authentic products and internal standard. [b] Corrected for BuBu from cuprate preparation (see text).