quantitatively, and none of the oxidized product was detected by NMR spectra and TLC analysis.

Quenching of Photosensitized Oxygenation of Diethyl Sulfide. A chloroform–methanol (5:1) solution of diethyl sulfide (1.6×10^{-2} M) and rose bengal (RB, 2.5×10^{-5} M) in the absence or presence of the quencher (1.1×10^{-3} M) was saturated with oxygen, and the system was closed and irradiated. At constant time intervals, the amount of absorbed oxygen was measured by using a buret in the closed system. The results obtained are shown in Figure 1.

Photosensitized Oxygenation of DPBF. Stock solution of RB (2 mL, 3.5×10^{-3} M) in methanol and 8 mL of freshly prepared DPBF with 2-pyrazoline or hydrazone (variable concentrations of DPBF to constant concentrations of 2-pyrazoline or hydrazone) in methanol–benzene (3:2) were mixed in Pyrex reaction tubes. After irradiation for a constant time (4 min) under oxygen bubbling, the internal standard, 9,10-diphenylanthracene (DPA), was added, and the reaction mixture was immediately analyzed by GLC. Analytical conditions were as follows: 4 mm × 1 m glass column, 10% SF-96 on Chromosorb, column temperature 200 °C; Hitachi 164 gas chromatograph with an FID detector. The yields of produced DBB were determined by comparison of the peak areas with that of the internal standard (DPA).

Photosensitized Oxygenation of 2-MP. For the determination of the product alcohols in RB-photosensitized oxygenation of 2-MP, gas chromatographic separation of the alcohols was carried out on an Ohkura gas chromatograph, Model 802 (6 mm × 1.5 m stainless steel column, 10% Carbowax 20M on Celite 545), after the photooxygenated mixture was reduced with an excess amount of dimethyl sulfide overnight. Two alcohols were separated, 4-methyl-2-penten-4-ol [oil; IR (NaCl) 3380 cm^{-1} (OH); ^{1}H NMR δ 5.53 (m, 2 H), 2.10 (br s, 1 H), 1.67 (d, 3 H, $J = 6.0$ Hz), 1.20 (s, 6 H)] and 2-methyl-1-penten-3-ol: oil; IR (NaCl) 3370 cm^{-1} (OH); ^{1}H NMR δ 4.80 (d, 2 H), 4.10 (t, 1 H, $J = 6.2$ Hz), 2.10 (s, 3 H), 1.63 (dq, 2 H, $J = 6.2$, 7.0 Hz), 1.20 (t, 3 H, $J = 7.0$ Hz).

Stock solution of RB (5 mL, 3.9×10^{-4} M) in methanol, 5 mL of freshly prepared 2-MP, and 5 mL of 2-pyrazoline or hydrazone (variable concentrations of 2-MP to constant concentrations of 2-pyrazoline or hydrazone) in methanol–benzene (3:2) were mixed in the Pyrex reaction tubes. After irradiation for a constant time (10 min), the reaction mixture was reduced with an excess of dimethyl sulfide and allowed to stand for 6 h, and the internal standard (cyclohexanone) was added to the reaction mixture and analyzed by GLC. Analytical conditions were as follows: 4 mm × 2 m glass column, 10% Carbowax 20M on Celite 545, column temperature 80 °C. The yields of alcohols were determined by the comparison of the peak areas with that of the internal standard.

Registry No. **1**, 742-01-8; **2**, 84237-85-4; **3**, 10180-07-1; **4**, 2256-22-6; **5**, 2515-62-0; **6**, 2256-18-0; **7**, 2564-18-3; **8**, 57609-72-0; **9**, 68189-23-1; RB, 11121-48-5; diethyl sulfide, 352-93-2; 1,3-diphenylisobenzofuran, 5471-63-6; 2-methyl-2-pentene, 625-27-4; O_2, 7782-44-7.

Chemistry of Higher Order, Mixed Organocuprates. 5.[1] On the Choice of the Copper(I) Salt for the Formation of R_2CuLi

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Received July 20, 1982

Chemical and spectroscopic studies are presented that have been designed to manifest differences in reagent composition and reactivity between mixtures of CuI/2RLi and CuSCN/2RLi. The results indicate that while both Cu(I) salts are reported to serve as precursors to lower order cuprates R_2CuLi, CuSCN may actually be forming a higher order, mixed species $R_2Cu(SCN)Li_2$. This would explain the discrepancy in coupling reactions of each solution with similar organic substrates under otherwise identical conditions. The presence of added lithium salts demonstrates that while LiI added to CuSCN/2RLi has essentially no effect, introduction of an equivalent of LiSCN to CuI/2RLi dramatically alters the efficiency of ligand transfer.

Introduction

Some 30 years ago, Gilman described[3] the first preparation of Me_2CuLi, **1**, an example of a class of organocopper compounds of general formula R_2CuLi that have come to be known as Gilman reagents. In this original report it was stated that either copper(I) halides or cuprous thiocyanate (CuSCN), upon addition of 2 equiv of MeLi in Et_2O, led to solutions of **1**. In the course of our studies on the nature[4] and synthetic potential[5] of higher order, mixed cuprates $R_2Cu(CN)Li_2$, **2**, it has been demonstrated not unexpectedly that in their preparation the Cu–CN moiety remained intact as shown by infrared spectroscopy. This lack of simple metal–metal exchange (i.e., $RLi + CuCN \nrightarrow RCu + LiCN$) may be attributed to the likelihood of dπ backbonding.[6] We were curious as to how a Cu(I) salt containing a related nontransferable ligand L [i.e., $R_2Cu(L)Li_2$, $L \neq CN$] would affect the reactions of higher order reagents relative to **2**. Thiocyanate was selected and led us to examine the possibility that the combination of 2RLi plus CuSCN might lead to a higher order species $R_2Cu(SCN)Li_2$, **3**, rather than a lower order Gilman cuprate. Herein we describe both chemical and spectroscopic data designed to elucidate the nature of the reagents so formed and point to the care that must be exercized in choosing a source of Cu(I) en route to the preparation of "R_2CuLi", **4**.

Results and Discussion

It was anticipated, should CuSCN lead to **3**, that a difference in chemical reactivity between a lower and

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[1] Part 4: Lipshutz, B. H.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 4696.

[2] Recipient of an American Cancer Society Junior Faculty Research Award, 1981–1983.

[3] Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630.

[4] Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S., manuscript in preparation.

[5] (a) Secondary halides: Lipshutz, B. H.; Wilhelm, R. S.; Floyd, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 7672. (b) Epoxides: Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. **Ibid. 1982**, *104*, 2305. (c) Enones: Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. *Tetrahedron Lett.* **1982**, *23*, 3755.

[6] Cotton, F. A.; Wilkinson, G. In "Advanced Inorganic Chemistry", 3rd ed.; Interscience, New York, 1972.

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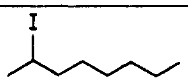
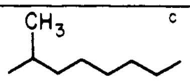
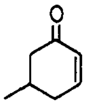
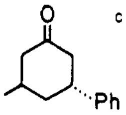
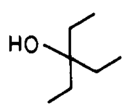
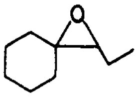
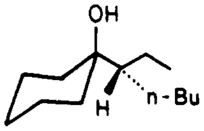
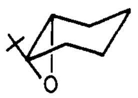
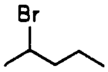
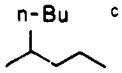
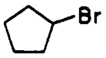
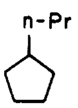
Table I. Comparison of Reagents Formed from CuI/2 RLi and CuSCN/2 RLi

entry	substrate	reagent composition (equiv)	conditions	product[a]	yield, %[b]
1		(a) CuI/2 CH_3Li (2) (b) CuSCN/2 CH_3Li	THF, 0 °C, 3 h	 [c]	99 91 (8)[d]
2		(a) CuI/2 PhLi (2) (b) CuSCN/2 PhLi	Et_2O, −78 °C, 1 h	 [c]	74 89
3	 **5**	(a) CuI/2 CH_3Li (1) (b) CuSCN/2 CH_3Li	THF, −40 °C, 2 h	 [c]	34 (33)[d] 42 (79)[d]
4	 **6**	(a) CuI/2 *n*-BuLi (1) (b) CuSCN/2 *n*-BuLi	THF, −20 °C, 6 h		18 (82)[d] 15 (79)[d]
5		(a) CuI/2 *n*-BuLi (2) (b) CuSCN/2 *n*-BuLi	THF, 0 °C, 5 h	[e]	
6		(a) CuI/2 *n*-BuLi (2) (b) CuSCN/2 *n*-BuLi	THF, 0 °C, 3 h	 [c]	10-14 (29)[d] 51-63 (6)[d]
7	 **7**	(a) CuI/2 *n*-PrLi (2) (b) CuSCN/2 *n*-PrLi	THF, 0 °C, 5 h	 [c]	14-24 44-56

[a] All products gave satisfactory IR, NMR, and mass spectral data. [b] By VPC analysis. [c] Product compared with an authentic sample (by VPC co-injection). [d] Percent recovered starting material. [e] No reaction occurred.

higher order species (i.e., **4** vs. **3**, respectively) would be apparent. Hence, a variety of substrates were treated with mixtures of CuI/2RLi and CuSCN/2RLi. While in the case of R = Me both reagents were clear, colorless to light tan-yellow solutions, switching to other alkyllithiums led to a noticeable difference between the two mixtures. With CuI dark solutions were formed, which may be a reflection on the reported thermal instability of many lower order cuprates.[7] Those formed from CuSCN, however, remained a clear, light tan-brown in color. This is precisely what has been observed with **2**, which have been shown to be both highly reactive yet far more thermally stable relative to their conventional predecessors **4**.[5]

Substrates added to each vessel of presumably similar content include epoxides, an enone, and three alkyl halides. The results are illustrated in Table I. Initially we focused on 2-iodooctane, which afforded the product of substitution in both cases in close to quantitative yields. This was not that surprising as **1** is a well-behaved, relatively stable dialkylcuprate.[7] Switching to an enone (entry 2) it was reasoned might reflect a difference in both product yield and possibly isomer ratios. As seen in Table I, the yield realized from the CuSCN/2PhLi reaction (entry 2) was 15% higher than when CuI/2PhLi was used. The ratio of isomers for each experiment, however, was comparable (ca. 98:2).

We next turned our attention to reactions of epoxides. A 1,1-disubstituted case (entry 3) led to only an 8% higher yield of product when using CuSCN vs. CuI. A trisubstituted oxirane (entry 4) likewise afforded similar results by using reagents derived from *n*-BuLi. The hindered *tert*-butylcyclohexene oxide (entry 5) gave no reaction (starting material recovered) in both cases.

While these data suggest that to some degree there are differences between CuI- and CuSCN-derived cuprates, more statistically meaningful examples were deemed necessary. From our experience on reactions of CuCN-based reagents with secondary unactivated bromides,[5a] it was surmised that this type of coupling partner would most clearly point to any existing dissimilarities in reactivity patterns. In the event, reaction of each reagent with 2-bromopentane (entry 6) led, in one case, to a 10–14% yield of product (i.e., 4-methyloctane) from the CuI-initiated cuprate, while a 51–63% yield of this same material was seen when CuSCN/2*n*-BuLi. Similarly, bromocyclopentane (entry 7) afforded only 14–24% *n*-propylcyclopentane (from CuI/2*n*-PrLi), in contrast to the 44–56% yields realized from the CuSCN-derived species. These chemical results would tend to substantiate our hypothesis that reaction of 2RLi with CuSCN gives rise to a reagent of composition different from that formed by using CuI. Low-temperature NMR spectra of both CuI/2MeLi and CuSCN/2MeLi were recorded under otherwise identical conditions of temperature (−19 °C), solvent composition (THF:Et_2O), and molarity (0.44 M) to fortify the experimental data presented above. Comparison of the spectrum for each shows a distinctly different methyl signal present. Me_2CuLi gives a singlet at δ 1.40,[8,9] while the peak for the

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(7) Posner, G. H. *Org. React.* **1975**, *22*, 253.

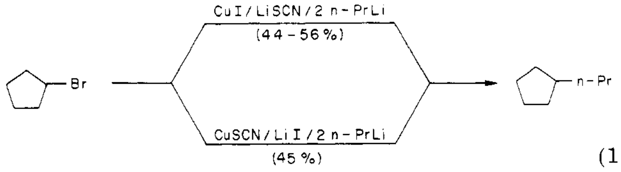
(8) This is in agreement with earlier NMR studies on this species; see: House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. House, H. O.; Fischer, W. F. *Ibid.* **1968**, *33*, 949. House, H. O.; Chu, C. Y. *Ibid.* **1976**, *41*, 3083. San Filippo, J. *Inorg. Chem.* **1978**, *17*, 275.

CuSCN-based reagent comes at slightly higher field (δ 1.45). An upfield shift, as in the CuSCN case, is characteristic of higher order cuprates[4,10] and is presumably due to the presence of an additional electron-rich ligand (i.e., SCN) bound to the copper center. This contrasts with the most current model[11] for **4**, where two R groups are associated with each copper atom in a dimeric[9] cluster.

Although these spectra were carefully recorded at 100 MHz with CH_2Cl_2 (capillary insert) as an internal standard, a difference in chemical shift of only 0.05 ppm, while readily discerned, is not as clear-cut as had been hoped for. Even preparing each solution independently, combining them into a single pot, and then recording the proton spectrum did not result in the appearance of two peaks between the temperature range −20 and −75 °C. This may be a case of fortuitous overlap, although the possibility that a rapid exchange of ligands is occurring, even at −75 °C, cannot be ruled out. This particular result, while disappointing, forced us to consider other chemical and spectroscopic methods that might provide additional supporting data.

In the preparation of the reagents it is clear that each solution must necessarily contain different species (e.g., CuI + 2RLi gives rise to 1 equiv of LiI which is not present when CuSCN is used) irrespective of the nature of the cuprate formed. Although the experimental parameters involved in reagent preparation were closely monitored, the presence of different salts (e.g., LiI from CuI, potentially LiSCN from CuSCN) could account for the chemical differences described. To evaluate the effects of lithium salts in solution, we decided to compare the reaction of CuI/2RLi + LiSCN with CuSCN/2RLi + LiI. In principle, each of these mixtures should afford similar chemical results, assuming similar reagents are involved when the additional lithium salts are present. If the addition of LiSCN to "R_2CuLi" significantly increased the yield of product relative to "R_2CuLi" alone, then this would strongly suggest that a modified reagent had been formed. Added LiI to the CuSCN/2RLi reagent, however, would be expected to have a negligible effect. Furthermore, infrared spectra on these two solutions should likewise show nearly identical cyanide stretching, which would corroborate any similarity found in chemical studies.

To investigate our hypothesis, we chose cyclopentyl bromide, **7**, as substrate so that the results obtained in the presence of added lithium salts could be compared directly with data already in hand (Table I, entry 7). Addition of 2 equiv of *n*-PrLi to a 1:1 mixture of CuI/LiSCN in THF, initially at −78 °C and then at 0 °C for 5 min, produced a clear solution (eq 1).[12] To this was added **7** (1 equiv) and the reaction allowed to proceed at this temperature for 5 h. Quenching and VPC analysis indicated that the yield of *n*-propylcyclopentane had jumped from 14–24% to 44–56%! On the other hand, when 1 equiv of LiI was added to CuSCN/2*n*-PrLi in THF, followed by 1 equiv of **7**, VPC analysis after the same period of time showed essentially identical results found wherein only CuSCN/2*n*-PrLi was used. The dramatic 2-fold increase in product formation due to the presence of added thiocyanate ion in solutions of "*n*-Pr_2CuLi" strongly suggests that different organcopper clusters are involved.



(1)

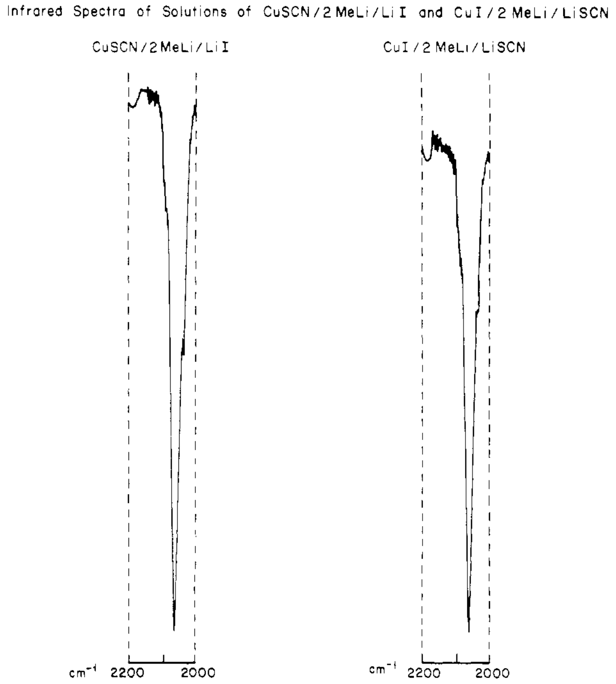


Figure 1. Infrared spectra of solutions of CuSCN/2MeLi/LiI and CuI/2MeLi/LiSCN.

To further substantiate these chemical tests, we investigated the solution IR spectrum for each reagent preparation. In full agreement with the similarity of product yields, essentially identical spectra (Figure 1) were obtained from solutions of both CuI/2MeLi/LiSCN and CuSCN/2MeLi/LiI (ν_{CN} 2065 cm^{-1}). Not only does this particular observation fit the existing chemical data, but it implies that thiocyanate ion is most likely bound to copper via sulfur rather than nitrogen.[13] This is plausible because (1) copper is in that "borderline region" of transition metals that can form either linkage isomer[15] and (2) Pearson's hard and soft acids and bases theory predicts thiocyanate (soft) rather than isothiocyanate (hard) to be bonded to

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[9] Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.

[10] Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312.

[11] Stewart, K. R.; Lever, J. R.; Whangbo, M. H. *J. Org. Chem.* **1982**, *47*, 1472.

[12] The observation that addition of *n*-propyllithium to CuI affords initially dark solutions of presumably *n*-Pr_2CuLi while the same preparation in the presence of LiSCN gives clear, just slightly yellowish solutions of reagent points to the effect of this salt on reagent composition and relative stability.

[13] The nature of the metal-ligand bonding has been qualitatively determined by the method of Burmeister et al.[14] Since the IR spectra of both CuI/2MeLi/LiSCN and CuSCN/2MeLi/LiI were essentially of equal intensity at identical concentrations, we repeated the CuSCN-based preparation with and without LiI. These were then compared with that of the standard, 1,4-dicyanobenzene (DCB), which was recorded at the same concentration and solvent composition as with the copper reagents. The integrated absorption intensities (IAI) for both of the mixtures and standard were calculated, from which the "internal" standard ratios (ISR) were determined. Due to the reactivity of the reagents toward DCB at temperatures at which the spectra were taken (i.e., room temperature or above), it was not valid to use DCB "internally" so as to get quantitative data. ISR values of <10 are known to denote metal (M)–SCN complexes while ratios >20 are indicative of M–NCS bonding. Calculations based on our spectra gave ISR values of 5.65 for the CuSCN/2MeLi case, while 7.53 was found with the same mixture in the presence of 1 equiv of LiI. Both results are well within the range of literature values and are highly suggestive of metal to sulfur bound reagents.

[14] Fultz, W. C.; Burmeister, J. L.; MacDougall, J. J.; Nelson, J. H. *Inorg. Chem.* **1980**, *19*, 1085.

[15] For a discussion, see: Huheey, J. E. In "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper and Row: New York, 1972; pp 406–415. Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 615–619.

copper(I) (soft).[16] A reasonable explanation for all of the data above is that CuSCN/2RLi forms, by analogy with CuCN, a higher order mixed cuprate of general formula $R_2Cu(SCN)Li_2$, which accounts for the considerably better coupling processes cited in Table I, particularly in entries 6 and 7. Upon admixture of 2RLi with CuI/LiSCN, the higher order reagent $R_2Cu(SCN)Li_2$ may form directly according to eq 2,[12,17] the presence of LiI being of little or no consequence.

$$\mathrm{CuI} + \mathrm{LiSCN} \xrightarrow[\mathrm{THF}]{2\mathrm{RLi}} \mathrm{R_2Cu(SCN)Li_2} + \mathrm{LiI} \tag{2}$$

Conclusions

Evidence has been presented supporting the original proposal that CuI and CuSCN form distinct reagents upon treatment of each with 2 equiv of RLi. The extent to which product yields vary with each species is a function of the substrate. Enones and disubstituted epoxides tended to afford somewhat higher yields with use of CuSCN/2RLi. The discrepancy in reagent constitution is most vividly observed where more challenging secondary, unactivated bromides are involved. In two cases the CuSCN-based cuprates led consistently to significantly greater product yields over those realized with the CuI/2RLi system. In the presence of added lithium salts (iodide and thiocyanate), which provide common ions within each reagent prepared, remarkable improvements in substitution reactions of lower order cuprates are observed. That is, in the specific case of bromocyclopentane examined, added LiSCN to "n-Pr_2CuLi" doubled the yield obtained with use of n-Pr_2CuLi alone, affording the same result seen with the CuSCN/2RLi system. The presence of LiI in either reaction mixture has no effect on the reaction pathway.

Low-temperature NMR experiments unfortunately did not provide unequivocal evidence as to the individuality of each organocopper reagent. Infrared studies, however, did confirm that solutions of CuI/2RLi/LiSCN and CuSCN/2RLi/LiI do resort to the same chemical blend, apparently with the thiocyanate ligand bound via sulfur to copper.

Thus, earlier reports,[18] wherein CuSCN/2RLi are claimed as a source of "R_2CuLi", in actuality were likely utilizing a higher order, mixed organocuprate as the reactive species. Whether $R_2Cu(SCN)Li_2$ are the actual (monomeric?) species responsible for the differences in chemistry observed vs. R_2CuLi is not certain nor critical at this time. Rather, this investigation does serve (1) as a caveat with regard to interpretation and expectations based on earlier reports using CuSCN as a precursor to Gilman reagents,[18] (2) to illustrate the potential for different Cu(I) salts to form unique reagents, and (3) to generate new avenues for future studies based on higher order copper reagents.[12,17]

Experimental Section

All glassware and syringes were dried in an oven (120 °C) overnight prior to use. Ethereal solvents (Et_2O, THF) were freshly distilled from sodium/benzophenone. Methyllithium was purchased from Aldrich, while n-butyllithium and phenyllithium were purchased from Ventron; n-propyllithium was prepared from n-propyl chloride;[19] vinyllithium was obtained from Organometallics; all lithium reagents were titrated by the method of Watson and Eastham.[20] Cuprous thiocyanate was purchased from Fisher and used without purification following storage in an Abderhalden over KOH under high vacuum at 56 °C overnight. Lithium thiocyanate (Ventron) was dried under high vacuum for 2 days (80 °C) prior to use. Lithium iodide (Ventron) was dried in an Abderhalden over KOH under high vacuum at 56 °C for 2 days prior to use. Cuprous iodide (Fisher) was purified by recrystallization from dimethyl sulfide as described by Floyd.[21] Experiments using different batches of CuI afforded results within experimental error. n-Propylcyclopentane was obtained from Sigma.

All variable-temperature ^1H NMR experiments were conducted on a Varian XL-100 NMR spectrometer. The capillary insert used contained ca. 10% CH_2Cl_2 in acetone-d_6. Solution infrared spectra were obtained with a Perkin-Elmer model 283 infrared spectrophotometer.

VPC analyses were conducted on a Hewlett-Packard Model 5880 A gas chromatograph. All runs were carried out with a 6 ft × $^1/_8$ in. column packed with 20% SE 30 on Chromosorb W.

TLC analyses were conducted with 0.25 mm glass SiO_2 or silica gel plates purchased from Baker. Column chromatography was performed by using Silica Gel-60 from Merck, 70–230 mesh.

Typical Procedure Using CuSCN/2RLi. Reaction of CuSCN/2*n*-BuLi with 6. Cuprous thiocyanate (0.0608 g, 0.50 mmol) was placed in a 25-mL two-neck round-bottom flask, evacuated with a vacuum pump and purged with argon. The process was repeated three times followed by addition of THF (1.0 mL). The resulting slurry was cooled to −78 °C, where n-butyllithium (0.4 mL, 1.0 mmol, 2.5 M) was added dropwise. Subsequent warming to 0 °C produced a light brown clear solution to which was added propylidenecyclohexane oxide (0.07 mL, 0.50 mmol) with stirring, via syringe. Stirring was continued for 6 h at −20 °C followed by quenching with 5 mL of a 9:1 saturated NH_4Cl/concentrated NH_4OH solution. VPC analysis indicated formation of 1-(3-heptyl)cyclohexan-1-ol (15%) vs. *tert*-butylcyclohexane as internal standard (corrected for response factors); IR (neat) 3465, 2930, 2860, 1460, 1450, 1375, 1155, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–0.8 (26 H, complex m); mass spectrum, m/e (relative intensity) 198 (M^+, 1.83), 181 (28.91), 142 (13.85), 125 (10.55), 111 (13.28) 99 (100.0); high-resolution mass spectrum calcd for $C_{13}H_{26}O$ 198.1984, found 198.1958.

Typical Procedure for Reactions of CuI/2RLi. Reaction of CuI/2*n*-BuLi with 6. Cuprous iodide (0.095 g, 0.49 mmol) was placed in a 25-mL two-neck round-bottom flask. The salt was evacuated with a vacuum pump followed by purging with argon, and the process was repeated three times. THF (1.0 mL) was added by syringe and the slurry cooled to −78 °C. n-Butyllithium (0.40 mL, 1.0 mmol, 2.5 M) was introduced dropwise, and the grey mixture was warmed to 0 °C, producing a black solution. At this temperature, propylidenecyclohexane oxide (0.07 mL, 0.50 mmol) was introduced dropwise neat via syringe. Stirring was continued for 6 h (−20 °C) followed by quenching with 5 mL of a 9:1 saturated NH_4Cl/concentrated NH_4OH solution. VPC analysis indicated formation of 1-(3-heptyl)cyclohexan-1-ol (18%) vs. *tert*-butylcyclohexane as internal standard (corrected for response factors).

Reaction of CuSCN/2MeLi with 5. 3-Ethyl-3-pentanol was formed in 42% yield by using the standard procedure for reactions of CuSCN/2RLi above, as shown by VPC analysis with 4-ethyl-3-hexanol as internal standard (corrected for response

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(16) Ho, T. L. In "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.

(17) In the course of our experiments where LiSCN was admixed with CuI (1 equiv) to which THF was added prior to introduction of the n-PrLi, we made an interesting, unexpected observation. Normally, CuI is slurried in THF as 2RLi is added to effect dissolution. Solubilization of CuI can be achieved by using phosphorous derivatives such as $(EtO)_3P$ or n-Bu_3P, which must be dry, distilled, and handled with care. Furthermore, they can complicate product isolation, usually requiring chromatographic separation. We have found that dry LiSCN will dissolve CuI in THF. Hence, not only may the need for phosphines be obviated, but in view of the results in this paper, use of LiSCN gives rise to a more reactive and efficient reagent. The generality of this new procedure for using LiSCN-solubilized CuI-derived cuprates is presently being investigated and will be described elsewhere.

(18) See, for example: Hartman, B. C.; Livinghouse, T.; Rickborn, B. *J. Org. Chem.* **1973**, *38*, 4346. Unfortunately, many earlier reports in communication form did not specify how the "R_2CuLi" used was prepared.

(19) See: Fieser; Fieser "Reagents in Organic Synthesis", Vol 5, p 283.

(20) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(21) Floyd, D. M. Ph.D. Thesis, University of Michigan, 1976, p 152.

factors); IR (neat) 3400, 2925, 2875, 1460, 1375, 1020, 960, 935 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (9 H, t), 1.5 (1 H, S), 1.50 (6 H, q); mass spectrum, *m/e* (relative intensity) 100 (20.84), 99 (100.0), 86 (54.48).

Reaction of CuI/2MeLi with 5. With use of the standard procedure for reactions of CuI/2RLi above, 3-ethyl-3-pentanol was formed in 34% yield.

Reaction of CuSCN/2PhLi with 3-Methylcyclohex-2-en-1-one. CuSCN (122 mg, 1.0 mmol) that had been dried under high vacuum in a drying pistol at 56 °C was placed in a dry two-neck flask and purged with argon. Dry Et_2O (1.0 mL) was introduced and the resulting slurry cooled to −78 °C. Phenyllithium (0.88 mL, 1.95 mmol, 2.22 M) was added via syringe, and the mixture was allowed to warm to 0 °C, at which point it became a yellowish orange, mostly homogeneous solution (small amount of solid was present). After 2–3 min at 0 °C the flask was recooled to −78 °C. 5-Methyl-2-cyclohexenone (0.052 mL, 0.5 mmol) was added, and the reaction mixture was allowed to stir at this temperature for 1 h. The mixture was then quenched at −78 °C with 6 mL of a 10% concentrated NH_4OH/90% saturated NH_4Cl solution followed by extractive workup (Et_2O) and drying ($MgSO_4$). Product was identified by VPC comparison with 3-methyl-5-phenylcyclohexanone, prepared earlier via reaction of $Ph_2Cu(CN)Li_2$ on the same substrate[5c] under similar conditions, which had been characterized by TLC, ^{1}H NMR, ^{13}C NMR, IR, and mass spectral data. GC/MS indicated a mixture of isomers. VPC with a 50 ft OV-101 capillary column indicated a 98:2 ratio of trans:cis isomers, in a combined yield of 89% relative to cyclohexanone as internal standard.

Reaction of CuI/2PhLi with 3-Methylcyclohex-2-en-1-one. 3-Methyl-5-phenylcyclohexanone, 74% yield, was formed by using the same quantities and procedure as described above in the reaction of CuSCN/2PhLi on the same substrate, 3-methylcyclohex-2-en-1-one, substituting CuI for CuSCN. VPC analysis on a 50 ft OV-101 capillary column indicated a 98:2 ratio of trans:cis isomers.

Reaction of CuSCN/2MeLi with 2-Iodooctane. CuSCN (122 mg, 1.0 mmol) was placed in a dry 25-mL two-neck flask under Ar. The system was successively evacuated under vacuum and purged with Ar three times. THF (1.0 mL) was introduced and the slurry cooled to −15 °C. Ethereal MeLi (1.48 mL, 2.0 mmol, 1.35 M, low halide) was added dropwise, producing an essentially clear, homogenous pale yellow solution. 2-Iodooctane (0.091 mL, 0.5 mmol) was then introduced (neat) via syringe and the reaction warmed to 0 °C, where it was maintained for 3 h. The solution was then quenched with a 9:1 mixture of saturated NH_4Cl/concentrated NH_4OH. VPC analysis indicated a 91% yield of 2-methyloctane (co-injection with authentic sample) vs. *tert*-butylcyclohexane as internal standard (along with 8% recovered starting material).

Reaction of CuI/2MeLi with 2-Iodooctane. A yield of 99% was indicated by VPC analysis following the typical procedure for reactions of CuI/2RLi.

Reaction of CuSCN/2*n*-BuLi with 2-Bromopentane. *n*-Butyllithium (0.80 mL, 2.0 mmol, 2.5 M) was introduced dropwise (−78 °C) to a slurry of THF (1.0 mL) and CuSCN (0.1216 g, 1.0 mmol) under argon. Following warming to 0 °C, a light brown clear solution resulted, which was recooled to −70 °C prior to the addition of 2-bromopentane (0.062 mL, 0.5 mmol). Immediate warming to 0 °C produced no visible change with stirring continued at the same temperature for 3 h. Quenching (5 mL of a 9:1 saturated NH_4Cl/concentrated NH_4OH solution) was followed by VPC analysis, which indicated formation of 4-methyloctane (co-injection with an authentic sample; 63%) vs. *tert*-butylcyclohexane as internal standard.

Reaction of CuI/2*n*-BuLi with 2-Bromopentane. 4-Methyloctane was formed in 14–24% yield by using the standard procedure for reactions of CuI/2RLi described above.

Reaction of CuI/LiSCN/2*n*-PrLi with Bromocyclopentane (7). Cuprous iodide (0.190 g, 1.0 mmol) was placed in a 25-mL two-neck round-bottom flask and purged with argon. The flask was transferred to a glovebox (under N_2) where lithium thiocyanate (0.066 g, 1.0 mmol) was added. The mixture of salts was then evacuated with a vacuum pump followed by purging with argon, with the process repeated three times. THF (2.4 mL) was then introduced, which dissolved the mixture of salts. The light yellow solution was cooled to −78 °C (pot goes heterogeneous) and *n*-propyllithium (1.01 mL, 2.0 mmol, 1.97 M) was added dropwise. A thick slurry resulted, which turned to a yellow solution upon warming to 0 °C. Cyclopentyl bromide (0.054 mL, 0.50 mmol) was introduced at this temperature, which was maintained for 5 h. Quenching (5 mL of a 9:1 saturated NH_4Cl/concentrated NH_4OH solution) followed by VPC analysis indicated formation of *n*-propylcyclopentane (co-injection with an authentic sample) in 44–56% yield (range of trials) vs. *tert*-butylcyclohexane as internal standard (corrected for response factors).

NMR Spectra: CuI/2MeLi; CuSCN/2MeLi; CuI/2MeLi + CuSCN/2MeLi. Cuprous thiocyanate (0.061 g, 0.5 mmol) was placed in a 25-mL two-neck round-bottom flask, evacuated with a vacuum pump, and purged with argon. The procedure was repeated three times before introduction of THF (0.65 mL). The resulting slurry was cooled to −78 °C, and methyllithium (0.49 mL, 1.0 mmol, 2.04 M) was added dropwise. Warming to 0 °C produced a tan solution within 5 min.

Me_2CuLi was prepared as a clear colorless solution as above with CuI (0.095 g, 0.5 mmol) in place of CuSCN.

Samples from the two reaction vessels were each transferred via cannula under argon to a dry NMR tube each equipped with a CH_2Cl_2/acetone-d_6 capillary insert, and the spectrum of each was recorded immediately thereafter. The remaining Me_2CuLi was then transferred via cannula into the flask containing the residual solution of CuSCN/2MeLi at 0 °C. After stirring for 1 h at this temperature, the mixture was transferred via cannula to a dry NMR tube equipped as above, and the NMR spectrum was immediately taken.

Acknowledgment. Financial support from the National Institutes of Health (GM 28128), the American Cancer Society (JFRA 37 to B.H.L.), and (in part) the Committee on Research, UCSB, is gratefully acknowledged. We also thank Professors Bruce Rickborn and William Kaska for helpful discussions.

Registry No. **5**, 1192-17-2; **6**, 28256-59-9; **7**, 137-43-9; CuI, 7681-65-4; CH_3Li, 917-54-4; CuSCN, 1111-67-7; PhLi, 591-51-5; *n*-BuLi, 109-72-8; *n*-PrLi, 2417-93-8; 2-iodooctane, 557-36-8; 5-methylcyclohex-2-en-1-one, 7214-50-8; 2-bromopentane, 107-81-3; 2-methyloctane, 3221-61-2; 3-methyl-5-phenylcyclohexanone, 28467-40-5; 3-ethyl-3-pentanol, 597-49-9; 1-(3-heptyl)cyclohexan-1-ol, 84370-47-8; 4-methyloctane, 2216-34-4; *n*-propylcyclopentane, 2040-96-2.