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Registry No.—**6**, 62777-57-5; **7a**, 62743-67-3; **8b**, 62743-68-4.

References and Notes

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Reactions of New Organocuprates. 2.[1] Substitution Reactions of Alkyl, Cycloalkyl, and Aryl Halides with $LiCu_2(CH_3)_3$, $Li_2Cu(CH_3)_3$, and $Li_2Cu_3(CH_3)_5$

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The new cuprates $LiCu_2(CH_3)_3$, $Li_2Cu(CH_3)_3$, and $Li_2Cu_3(CH_3)_5$ in Et_2O and THF have been compared to $LiCu(CH_3)_2$ and CH_3Li in their reaction toward alkyl, cycloalkyl, and aryl halides (where halogen = I, Br, Cl, F). In most cases the new cuprate $Li_2Cu(CH_3)_3$ was superior to all other reagents and in some cases the superiority was substantial.

We have recently obtained evidence for the existence of the new organocuprate species, $LiCu_2(CH_3)_3$ and $Li_2Cu(CH_3)_3$ in THF and $Li_2Cu(CH_3)_3$ and $Li_2Cu_3(CH_3)_5$ in Et_2O.[2] We have also reported the reactions of these new organocuprates with enones in order to compare their regioselectivity and reaction rate with $LiCu(CH_3)_2$.[1] Owing to the current interest in substitution reactions using organocopper reagents,[3] we have now evaluated these new cuprates in their reaction with alkyl, cycloalkyl, and aryl halides and have noted some interesting and important observations.

Results and Discussion

The organic halides were allowed to react with the new organocuprates and $LiCu(CH_3)_2$ in THF and Et_2O in order to compare the reactivity of the new cuprates and the yields of the reactions. Since $Li_2Cu(CH_3)_3$ is in equilibrium with $LiCu(CH_3)_2$ and CH_3Li, the reaction of CH_3Li in each case is also compared. Each reaction was carried out using excess reagent (10:1 molar ratio of active methyl:halide), room temperature, and two solvents (THF and Et_2O). Since $LiCu_2(CH_3)_3$ is insoluble in Et_2O and $Li_2Cu_3(CH_3)_5$ is insoluble in THF, studies of these cuprates were not involved in these particular solvents. The results of these reactions are shown in Table I.

In the reactions of 1-iodododecane (expt 1–7), each organocuprate reagent reacted similarly to produce the substitution product, *n*-undecane, in high yield. The earlier reaction time (10 min) indicated that $Li_2Cu(CH_3)_3$ in THF reacted more rapidly than any other reagent. The metal–halogen exchange to form 50% *n*-decane in the reaction of CH_3Li with 1-iododecane suggests that in reactions involving $Li_2Cu(CH_3)_3$, the reactive species is $Li_2Cu(CH_3)_3$ and not one of its equilibrium components (e.g., CH_3Li). Our previous studies have shown that $Li_2Cu(CH_3)_3$ forms an equilibrium mixture in THF and Et_2O as described by eq 1.

$$Li_2Cu(CH_3)_3 \rightleftharpoons CH_3Li + LiCu(CH_3)_2 \qquad (1)$$

Methyllithium as well as the cuprates also reacted with 1-bromodecane to form undecane. The yields in THF were quantitative after just 1 h reaction time (expt 8–14), although the yields were considerably lower (42–61%) in ether solvent. The reactione of1-chlorodecane (expt 15–21) illustrate the superiority of $Li_2Cu(CH_3)_3$ over $LiCu(CH_3)_2$ or $LiCu_2(CH_3)_3$ in THF or Et_2O in the substitution of chlorine for methyl. A quantitative yield was obtained with $Li_2Cu(CH_3)_3$, whereas with $LiCu(CH_3)_2$ in THF only 22% yield was observed and in the case of CH_3Li in THF, no reaction at all was observed under the same conditions. Although yields are low in all other cases studied involving reaction of the new cuprates and CH_3Li with 1-fluorodecane, a quantitative yield of *n*-undecane was observed when $Li_2Cu(CH_3)_3$ in ether was the reagent. It is interesting to note that whereas $Li_2Cu(CH_3)_3$ in THF is a superior reagent for chlorine displacement, the same reagent in Et_2O is superior for fluorine displacement (expt 22–28).

The reactions of 6-bromo-1-hexene and 6-chloro-1-hexene behaved similarly to 1-bromodecane and 1-chlorodecane (expt 29–40). In general, THF solvent is more suitable than Et_2O for organocuprate substitution reactions of alkyl iodides, bromides, and chlorides and the relative reactivity of the cuprates is $Li_2Cu(CH_3)_3$ > $LiCu(CH_3)_2$, $LiCu_2(CH_3)_3$, and $Li_2Cu_3(CH_3)_5$, although $Li_2Cu(CH_3)_3$ in Et_2O was superior to THF in its reaction with 1-fluorodecane (expt 26, 96%). Although CH_3Li also produced good yields of substitution products with the iodides and bromides, no reaction took place between CH_3Li and the chlorides and fluorides. In most cases the yield of substitution products is better using the new cu-

Table I. Substitution Reactions of Halides with $LiCu(CH_3)_2$, $LiCu_2(CH_3)_3$, $Li_2Cu(CH_3)_3$, $Li_2Cu_3(CH_3)_5$, and CH_3Li at Room Temperature

Expt	Cuprate reagent	Halide substrate	Reaction time and solvent	Product(s) (yield(s), %)
1	$LiCu(CH_3)_2$	1-Iododecane	10 min, THF	*n*-Undecane (57)
			1 h, THF	*n*-Undecane (100)
2	$LiCu_2(CH_3)_3$	1-Iododecane	10 min, THF	*n*-Undecane (65)
			1 h, THF	*n*-Undecane (104)
3	$Li_2Cu(CH_3)_3$	1-Iododecane	10 min, THF	*n*-Undecane (92)
			1 h, THF	*n*-Undecane (98)
4	$LiCu(CH_3)_2$	1-Iododecane	1 h, Et_2O	*n*-Undecane (106)
5	$Li_2Cu(CH_3)_3$	1-Iododecane	1 h, Et_2O	*n*-Undecane (76)
			3 h, Et_2O	*n*-Undecane (101)
6	$Li_2Cu_3(CH_3)_5$	1-Iododecane	1 h, Et_2O	*n*-Undecane (59)
7	CH_3Li	1-Iododecane	1 h, Et_2O	*n*-Undecane (30)
				n-Decane (50)
8	$LiCu(CH_3)_2$	1-Bromodecane	1 h, THF	*n*-Undecane (98)
9	$LiCu_2(CH_3)_3$	1-Bromodecane	1 h, THF	*n*-Undecane (96)
10	$Li_2Cu(CH_3)_3$	1-Bromodecane	1 h, THF	*n*-Undecane (96)
11	$LiCu(CH_3)_2$	1-Bromodecane	1 h, Et_2O	*n*-Undecane (42)
12	$Li_2Cu(CH_3)_3$	1-Bromodecane	1 h, Et_2O	*n*-Undecane (44)
13	$Li_2Cu_3(CH_3)_5$	1-Bromodecane	1 h, Et_2O	*n*-Undecane (61)
14	CH_3Li	1-Bromodecane	1 h, Et_2O	*n*-Undecane (95)
15	$LiCu(CH_3)_2$	1-Chlorodecane	12 h, THF	*n*-Undecane (22)
16	$LiCu_2(CH_3)_3$	1-Chlorodecane	12 h, THF	*n*-Undecane (60)
17	$Li_2Cu(CH_3)_3$	1-Chlorodecane	12 h, THF	*n*-Undecane (102)
18	$LiCu(CH_3)_2$	1-Chlorodecane	12 h, Et_2O	*n*-Undecane (14)
19	$Li_2Cu(CH_3)_3$	1-Chlorodecane	12 h, Et_2O	*n*-Undecane (37)
20	$Li_2Cu_3(CH_3)_5$	1-Chlorodecane	12 h, Et_2O	*n*-Undecane (30)
21	CH_3Li	1-Chlorodecane	12 h, Et_2O	*n*-Undecane (0)
22	$LiCu(CH_3)_2$	1-Fluorodecane	48 h, THF	*n*-Undecane (2)
23	$LiCu_2(CH_3)_3$	1-Fluorodecane	48 h, THF	*n*-Undecane (2)
24	$Li_2Cu(CH_3)_3$	1-Fluorodecane	48 h, THF	*n*-Undecane (8)
25	$LiCu(CH_3)_2$	1-Fluorodecane	24 h, Et_2O	*n*-Undecane (24)
26	$Li_2Cu(CH_3)_3$	1-Fluorodecane	24 h, Et_2O	*n*-Undecane (96)
27	$Li_2Cu_3(CH_3)_5$	1-Fluorodecane	24 h, Et_2O	*n*-Undecane (13)
28	CH_3Li	1-Fluorodecane	24 h, Et_2O	*n*-Undecane (0)
29	$LiCu(CH_3)_2$	6-Bromohexene	1 h, THF	1-Heptene (95)
30	$LiCu_2(CH_3)_3$	6-Bromohexene	1 h, THF	1-Heptene (105)
31	$Li_2Cu(CH_3)_3$	6-Bromohexene	1 h, THF	1-Heptene (108)
32	$LiCu(CH_3)_2$	6-Bromohexene	3 h, Et_2O	1-Heptene (88)
33	$Li_2Cu(CH_3)_3$	6-Bromohexene	3 h, Et_2O	1-Heptene (86)
34	CH_3Li	6-Bromohexene	1 h, THF	1-Heptene (93)
35	$LiCu(CH_3)_2$	6-Chloro-1-hexene	24 h, THF	1-Heptene (84)
36	$LiCu_2(CH_3)_3$	6-Chloro-1-hexene	24 h, THF	1-Heptene (75)
37	$Li_2Cu(CH_3)_3$	6-Chloro-1-hexene	24 h, THF	1-Heptene (95)
38	$LiCu(CH_3)_2$	6-Chloro-1-hexene	24 h, Et_2O	1-Heptene (68)
39	$Li_2Cu(CH_3)_3$	6-Chloro-1-hexene	24 h, Et_2O	1-Heptene (92)
40	CH_3Li	6-Chloro-1-hexene	24 h, Et_2O	1-Heptene (0)
41	$LiCu(CH_3)_2$	Iodocyclohexane	48 h, THF	Methylcyclohexane (21), cyclohexane (14)
42	$LiCu_2(CH_3)_3$	Iodocyclohexane	48 h, THF	Methylcyclohexane (5), cyclohexane (15)
43	$Li_2Cu(CH_3)_3$	Iodocyclohexane	48 h, THF	Methylcyclohexane (93), cyclohexane (5)
44	$LiCu(CH_3)_2$	Iodocyclohexane	48 h, Et_2O	Methylcyclohexane (68), cyclohexane (20)
45	$Li_2Cu(CH_3)_3$	Iodocyclohexane	48 h, Et_2O	Methylcyclohexane (53), cyclohexane (32)
46	CH_3Li	Iodocyclohexane	5 h, Et_2O	Methylcyclohexane (0), cyclohexane (97)
47	CH_3Li	Iodocyclohexane	48 h, THF	Methylcyclohexane (26), cyclohexane (10)
48	$LiCu(CH_3)_2$	Bromocyclohexane	48 h, THF	Methylcyclohexane (0), cyclohexane (0)
49	$LiCu_2(CH_3)_3$	Bromocyclohexane	48 h, THF	Methylcyclohexane (3), cyclohexane (0)
50	$Li_2Cu(CH_3)_3$	Bromocyclohexane	48 h, THF	Methylcyclohexane (3), cyclohexane (0)
51	$LiCu(CH_3)_2$	Bromocyclohexane	48 h, Et_2O	Methylcyclohexane (12), cyclohexane (0)
52	$Li_2Cu(CH_3)_3$	Bromocyclohexane	48 h, Et_2O	Methylcyclohexane (12), cyclohexane (4)
53	CH_3Li	Bromocyclohexane	48 h, Et_2O	Methylcyclohexane (0), cyclohexane (27)
54	$LiCu(CH_3)_2$	Chlorocyclohexane	48 h, THF	Methylcyclohexane (0), cyclohexane (0)
55	$LiCu_2(CH_3)_3$	Chlorocyclohexane	48 h, THF	Methylcyclohexane (0), cyclohexane (0)
56	$Li_2Cu(CH_3)_3$	Chlorocyclohexane	48 h, THF	Methylcyclohexane (0), cyclohexane (0)
57	$LiCu(CH_3)_2$	Chlorocyclohexane	48 h, Et_2O	Methylcyclohexane (0), cyclohexane (0)
58	$Li_2Cu(CH_3)_3$	Chlorocyclohexane	48 h, Et_2O	Methylcyclohexane (0), cyclohexane (0)
59	$LiCu(CH_3)_2$	Iodobenzene	14 h, THF	Toluene (91)
60	$LiCu_2(CH_3)_3$	Iodobenzene	14 h, THF	Toluene (91)
61	$Li_2Cu(CH_3)_3$	Iodobenzene	14 h, THF	Toluene (96)
62	$LiCu(CH_3)_2$	Iodobenzene	14 h, Et_2O	Toluene (82)
63	$Li_2Cu(CH_3)_3$	Iodobenzene	14 h, Et_2O	Toluene (92)
64	CH_3Li	Iodobenzene	14 h, Et_2O	Toluene (95)
65	$LiCu(CH_3)_2$	Bromobenzene	24 h, THF	Toluene (45)

Table I *(Continued)*

Expt	Cuprate reagent	Halide substrate	Reaction time and solvent	Products(s) (yield(s), %)
66	$LiCu_2(CH_3)_3$	Bromobenzene	24 h, THF	Toluene (0)
67	$Li_2Cu(CH_3)_3$	Bromobenzene	24 h, THF	Toluene (102)
68	$LiCu(CH_3)_2$	Bromobenzene	24 h, Et_2O	Toluene (59)
69	$Li_2Cu(CH_3)_3$	Bromobenzene	24 h, Et_2O	Toluene (61)
70	CH_3Li	Bromobenzene	24 h, Et_2O	Toluene (115)
71	$LiCu(CH_3)_2$	Chlorobenzene	24 h, THF	Toluene (65)
72	$LiCu_2(CH_3)_3$	Chlorobenzene	24 h, THF	Toluene (0)
73	$Li_2Cu(CH_3)_3$	Chlorobenzene	24 h, THF	Toluene (42)
74	$LiCu(CH_3)_2$	Chlorobenzene	24 h, Et_2O	Toluene (0)
75	$Li_2Cu(CH_3)_3$	Chlorobenzene	24 h, Et_2O	Toluene (47)
76	CH_3Li	Chlorobenzene	24 h, Et_2O	Toluene (33)
77	$LiCu(CH_3)_2$	Fluorobenzene	24 h, THF	Toluene (24)
78	$LiCu_2(CH_3)_3$	Fluorobenzene	24 h, THF	Toluene (0)
79	$Li_2Cu(CH_3)_3$	Fluorobenzene	24 h, THF	Toluene (49)
80	$LiCu(CH_3)_2$	Fluorobenzene	24 h, Et_2O	Toluene (0)
81	$Li_2Cu(CH_3)_3$	Fluorobenzene	24 h, Et_2O	Toluene (50)
82	CH_3Li	Fluorobenzene	24 h, THF	Toluene (21)
83	$LiCu(CH_3)_2$	*p*-Chloroanisole	48 h, THF	*p*-Methylanisole (0)
84	$LiCu_2(CH_3)_5$	*p*-Chloroanisole	48 h, THF	*p*-Methylanisole (0)
85	$Li_2Cu(CH_3)_3$	*p*-Chloroanisole	48 h, THF	*p*-Methylanisole (0)
86	$LiCu(CH_3)_2$	*p*-Chloroanisole	48 h, Et_2O	*p*-Methylanisole (0)
87	$Li_2Cu(CH_3)_3$	*p*-Chloroanisole	48 h, Et_2O	*p*-Methylanisole (21)
88	CH_3Li	*p*-Chloroanisole	48 h, Et_2O	*p*-Methylanisole (11) Anisole (8)
89	$LiCu(CH_3)_2$	*p*-Fluoroanisole	48 h, THF	*p*-Methylanisole (0)
90	$LiCu_2(CH_3)_2$	*p*-Fluoroanisole	48 h, THF	*p*-Methylanisole (0)
91	$Li_2Cu(CH_3)_3$	*p*-Fluoroanisole	48 h, THF	*p*-Methylanisole (83)
92	$LiCu(CH_3)_2$	*p*-Fluoroanisole	48 h, Et_2O	*p*-Methylanisole (3)
93	$Li_2Cu(CH_3)_3$	*p*-Fluoroanisole	48 h, Et_2O	*p*-Methylanisole (101)
94	CH_3Li	*p*-Fluoroanisole	48 h, Et_2O	*p*-Methylanisole (82)
95	$LiCu(CH_3)_2$	1-Chlorocyclohexene	48 h, THF	1-Methylcyclohexene (0)
96	$LiCu_2(CH_3)_3$	1-Chlorocyclohexene	48 h, THF	1-Methylcyclohexene (0)
97	$Li_2Cu(CH_3)_3$	1-Chlorocyclohexene	48 h, THF	1-Methylcyclohexene (0)
98	$LiCu(CH_3)_2$	1-Chlorocyclohexene	48 h, Et_2O	1-Methylcyclohexene (0)
99	$Li_2Cu(CH_3)_3$	1-Chlorocyclohexene	48 h, Et_2O	1-Methylcyclohexene (71)
100	CH_3Li	1-Chlorocyclohexene	48 h, Et_2O	1-Methylcyclohexene (0)
101	$LiCu(CH_3)_2$	3-Chlorocyclohexene	48 h, THF	3-Methylcyclohexene (57)
102	$LiCu_2(CH_3)_3$	3-Chlorocyclohexene	48 h, THF	3-Methylcyclohexene (33)
103	$Li_2Cu(CH_3)_3$	3-Chlorocyclohexene	48 h, THF	3-Methylcyclohexene (83)
104	$LiCu(CH_3)_2$	3-Chlorocyclohexene	48 h, Et_2O	3-Methylcyclohexene (58)
105	$Li_2Cu(CH_3)_3$	3-Chlorocyclohexene	48 h, Et_2O	3-Methylcyclohexene (62)
106	CH_3Li	3-Chlorocyclohexene	48 h, Et_2O	3-Methylcyclohexene (8)

prate $Li_2Cu(CH_3)_3$ than $LiCu(CH_3)_2$ and in many cases the difference in yield is substantial.

The reactions of iodocyclohexane (expt 41–47) are much slower than the reactions observed earlier with the primary alkyl iodides and in addition considerable metal–halogen interchange is observed. Once again the best substitution reaction was achieved in the reaction of iodocyclohexane with $Li_2Cu(CH_3)_3$ in THF (93% yield with 5% cyclohexane byproduct). Reaction of iodocyclohexane with other cuprates and CH_3Li produced substantial amounts of the metal–halogen interchange product, cyclohexane. Under the best conditions, bromocyclohexane (expt 48–53) gave only 12% yield in its reaction with $Li_2Cu(CH_3)_3$ whereas chlorocyclohexane (expt 54–58) showed no reaction with any of the reagents after 48 h. The halogen reactivity decreased in the order I > Br > Cl which is the same trend observed for primary halides.

Experiments 59–82 describe the results of the reactions of various cuprates with the halogenobenzenes in ether and THF. The substitution reactions of iodobenzene can be effected in good yields by each organocuprate studied or methyllithium itself. In the case of bromobenzene, both CH_3Li in ether and $Li_2Cu(CH_3)_3$ in THF caused quantitative substitution whereas the other cuprates were much less effective. The results involving chlorobenzene and fluorobenzene show moderate yields when $LiCu(CH_3)_2$, $Li_2Cu(CH_3)_3$ in THF, and $Li_2Cu(CH_3)_3$ in Et_2O are allowed to react. In each case CH_3Li gives significantly lower yields. Although it was not possible to determine the relative rate of reaction between $Li_2Cu(CH_3)_3$ and $LiCu(CH_3)_2$ in order to see if CH_3Li affects the substitution reaction as well as $LiCu(CH_3)_2$, the reactions of fluorobenzene, *p*-chloroanisole, and *p*-fluoroanisole (expt 83–94) show that $Li_2Cu(CH_3)_3$ is more reactive than $LiCu(CH_3)_2$ in THF or Et_2O in aryl halide substitution reactions. It is interesting that in the case of *p*-chloroanisole only $Li_2Cu(CH_3)_3$ and CH_3Li in ether produced any product at all and that was in very modest yield whereas *p*-fluoroanisole, when allowed to react with $Li_2Cu(CH_3)_3$ in ether, formed *p*-methylanisole in quantitative yield.

It is important to note that $Li_2Cu(CH_3)_3$ in Et_2O reacted with 1-chlorocyclohexene to yield 71% 1-methylcyclohexene whereas all other reagents had no effect on this alkenyl halide (expt 95–100). When the chlorine atom was placed in the allylic position (3-chlorocyclohexene) $Li_2Cu(CH_3)_3$ in THF had a significantly higher reactivity than the other cuprates (expt 101–106).

In conclusion, it has been shown that, in general, $Li_2Cu(CH_3)_3$ exhibits a higher reactivity than other cuprates in halide substitution reactions involving alkyl, cycloalkyl, and aryl halides. Also, $LiCu_2(CH_3)_3$ in THF and $Li_2Cu_3(CH_3)_5$ in Et_2O were considerably less effective than $LiCu(CH_3)_2$ or $Li_2Cu(CH_3)_3$ in the same reactions in most cases. Most often THF was the superior solvent, although in some cases ether was decidedly better. The superiority of $Li_2Cu(CH_3)_3$ over $LiCu(CH_3)_3$ and the other cuprates in most cases reported here indicates a potential for this reagent in other reactions not heretofore explored.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[4] Other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone to remove solents vapors.[5–7] ^1H NMR spectra were obtained at 60 MHz using a Varian A-60 NMR spectrometer.

Analytical. Active CH_3 group analysis was carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line and collecting the evolved methane with a Toepler pump.[5] Lithium was determined by flame photometry. Iodide was determined by the Volhard procedure. Copper was determined by electrolytic deposition on a Pt electrode.

Materials. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher Reagent) over $LiAlH_4$ prior to use. Methyllithium in THF and Et_2O was prepared by the reaction of $(CH_3)_2Hg$ with excess lithium metal. Both solutions were stored at −78 °C until ready to use. Cuprous iodide was purified by precipitation from an aqueous KI–CuI solution.[6] The precipitated solid was washed with water, ethanol, and diethyl ether and then dried at room temperature under reduced pressure.

Preparation of Reagents in THF. $LiCu_2(CH_3)_3$. Cuprous iodide (1.53 g, 8.05 mmol) was weighed into a 50-mL round-bottom flask in the drybox, then the flask fitted with a rubber septum. The flask was removed from the drybox and connected by means of a needle to a nitrogen bubbler, and 15 mL of THF was added in order to slurry the solid. The slurry was cooled to −78 °C and 15.1 mL of a 0.802 M solution of CH_3Li (12.1 mmol) in THF was added to the flask. Within 5 min all of the solid had dissolved and a clear, brown solution was present. ^1H NMR at −96 °C showed the solution to contain only $LiCu_2(CH_3)_3$.[2] Analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 1.49:1.00:1.50:1.02.

$LiCu(CH_3)_2$. Cuprous iodide (1.26 g, 6.62 mmol) was allowed to react with 16.5 mL of 0.802 M CH_3Li (13.2 mmol) in THF using the same procedure as was used to prepare $LiCu_2(CH_3)_3$ (see above). All the solid dissolved within 1 min to yield a clear, light-brown solution. ^1H NMR at −96 °C showed only one signal at δ 15.7, which corresponds to $LiCu(CH_3)_2$. An analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 2.00:1.00:2.12:0.98.

$Li_2Cu(CH_3)_3$. Cuprous iodide (0.80 g, 4.32 mmol) was allowed to react with 19.0 mL of 0.802 M CH_3Li (16.9 mmol) in THF using the above procedure for making $LiCu_2(CH_3)_3$. All the solid dissolved within 1 min to yield a clear, colorless solution. ^1H NMR at −96 °C showed the presence of $Li_2Cu(CH_3)_3$ in equilibrium with $LiCu(CH_3)_2$, and CH_3Li (four signals at δ −1.40, −1.57, −1.73, and −2.08 are observed; signals at δ −1.57 and −2.08 are due to $LiCu(CH_3)_2$ and CH_3Li, respectively, while those at δ −1.40 and −1.73 are due to $Li_2Cu(CH_4)_3$). An analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 3.82:1.00:3.62:0.94.

Preparation of Reagents in Et_2O. $LiCu(CH_3)_2$. Cuprous iodide (0.53 g, 2.79 mmol) was weighed into a 50-mL round-bottom flask in the drybox, then the flask fitted with a rubber septum. The flask was removed from the drybox and connected by means of a needle to a nitrogen bubbler, and 5 mL of Et_2O was added in order to slurry the solid. The slurry was cooled to −78 °C and 4.4 mL of 1.27 M solution of CH_3Li (5.58 mmol) in Et_2O was added to the flask. All the solid dissolved immediately and a clear, colorless solution formed. ^1H NMR at −96 °C showed only $LiCu(CH_3)_2$ to be present. An analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 1.97:1.00:0.96:0.95.

$Li_2Cu_3(CH_3)_5$. Cuprous iodide (0.380 g, 2.0 mmol) was allowed to react with 3.5 mL of a 0.95 M solution of CH_3Li (3.3 mmol) in Et_2O using the same procedure as was used to prepare $LiCu(CH_3)_2$ (see above). Most of the solid dissolved immediately to give a clear, light pink solution, but a small amount of a yellow solid (methylcopper) remained. An analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 5.21:3.00:5.09:3.03. If all of the iodide is assumed to be present as LiI, then the organocopper species would have a Li:Cu:CH_3 ratio of 2.18:3.00:5.09. This indicates the presence of the complex $Li_2Cu_3(CH_3)_5$. This compound was indeed shown to be present by NMR spectroscopy.[2]

$Li_2Cu(CH_3)_3$. Cuprous iodide (0.57 g, 2.97 mmol) was allowed to react with 9.36 mL of a 1.27 M solution of CH_3Li (11.9 mmol) in Et_2O using the same procedure as was used to prepare $LiCu(CH_3)_2$ (see above). All the solid dissolved immediately and a clear, colorless solution remained. ^1H NMR at −96 °C showed $Li_2Cu(CH_3)_3$, $LiCu(CH_3)_2$, and CH_3Li to be present.[2] An analysis of the solution showed Li, Cu, CH_3, and I to be present in the ratio 3.82:1.00:3.88:1.02.

General Reactions of Halides. A 10-mL Erlenmeyer flask with a Teflon-coated magnetic stirring bar was dried in an oven and allowed to cool under nitrogen, then sealed with a rubber septum and connected by means of a needle to a nitrogen-filled manifold equipped with a mineral oil filled bubbler. The cuprate reagent (ca. 0.1–0.5 mmol) was syringed into the flask and the calculated amount of halide substrate (in THF or Et_2O solvent with internal standard, n-$C_{12}H_{26}$ for n-decyl halides, n-C_8H_{18} for 6-bromo-1-hexene, 6-chloro-1-hexene, cyclohexyl halides, 1-chlorocyclohexene, and 3-chlorocyclohexene, p-xylene for benzyl halides) added to the stirred reagent. After the designated reaction time, the reaction mixture was quenched with H_2O slowly and dried over $MgSO_4$. A 10-ft column (5% Carbowax 20M on Chromosorb W) was used to separate the product of n-decyl halides (110 °C). A 6-ft column (10% Apiezon L 60-80S) was used to separate the products of 6-bromo-1-hexene, 6-chloro-1-hexene, cyclohexyl halides, 1-chlorocyclohexene, 3-chlorocyclohexene (55 °C), and benzyl halides (105 °C). Halide substrates and authentic samples of products were purchased commercially and the percent yield reported in Table I is the absolute yield based on halide substrate.

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Registry No.—$LiCu(CH_3)_2$, 15681-48-8; $LiCu_2(CH_3)_3$, 61303-82-0; $Li_2Cu(CH_3)_3$, 61278-42-0; $Li_2Cu_3(CH_3)_5$, 61701-36-8; CH_3Li, 917-54-4; 1-iododecane, 2050-77-3; 1-bromodecane, 112-29-8; 1-chlorodecane, 1002-69-3; 1-fluorodecane, 334-56-5; 6-bromohexene, 2695-47-8; 6-chloro-1-hexene, 928-89-2; iodocyclohexane, 626-62-0; bromocyclohexane, 108-85-0; chlorocyclohexane, 542-18-7; iodobenzene, 591-50-4; bromobenzene, 108-86-1; chlorobenzene, 108-90-7; fluorobenzene, 462-06-6; p-chloroanisole, 623-12-1; p-fluoroanisole, 459-60-9; 1-chlorocyclohexene, 930-66-5; 3-chlorocyclohexene, 2441-97-6.

References and Notes

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