Comparative Study of Some Selected Reactions of Homogeneous and Polymer-Supported Lithium Diorganocuprates

Robert H. Schwartz[1] and Joseph San Filippo, Jr.*

Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903

Received February 20, 1979

Solutions obtained by mixing 2 equiv of an organolithium reagent RLi (R = methyl, *n*-butyl, *sec*-butyl, *tert*-butyl, phenyl) with 1 equiv of polymer-bound iodo(triarylphosphine)copper(I) have been allowed to react with a representative series of alkyl halides, tosylates, and α,β-enones. In general, the resulting product yields are comparable or superior to those obtained with related homogeneous reagents. The use of such polymer-supported reagents eliminates a major drawback to the use of equivalent homogeneous reagents, viz., the inclusion of 1 or more equiv of tertiary phosphine or phosphite in the reaction mixture. An examination of the reaction of *sec*-butyl- and *tert*-butyllithium with a suspension of copper(I) iodide has revealed a dramatic solvent and temperature dependence: in contrast to the reagent prepared in ether, the equivalent reaction at 0 °C in THF produces a reagent which readily couples with alkyl halides and tosylates, thus extending the general utility of this synthetically useful procedure.

$$2RLi + CuI \xrightarrow[(2)\ R'X]{(1)\ THF,\ 0\ ^{\circ}C} R\text{-}R'\ (70\text{-}100\%)$$
$$R = sec\text{-}Bu,\ t\text{-}Bu;\ R' = \text{primary}$$

Lithium organocuprates, R_2CuLi, rank among the most synthetically useful of all organometallic reagents, providing broadly applicable procedures for the formation of carbon–carbon σ bonds.[2] Initial studies demonstrated the stability and subsequent utility that accompany the use of ether-soluble copper(I) halide–tertiary phosphine complexes (1) as convenient precursors to the requisite ate complexes (eq 1).[3] The resulting lithium diorganocuprates

$$2RLi + \underset{1}{XCu(L)} \rightarrow \underset{2}{R_2CuLi(L)} \qquad (1)$$
$$R = \text{primary, secondary, tertiary, vinyl, aryl}$$

(**2**) all couple with *n*-alkyl halides and tosylates in high yield (eq 2). The corresponding reaction with *sec*- or

$$R_2CuLi(L) + R'X \xrightarrow{THF} R\text{-}R'\ (\geq 90\%) \qquad (2)$$
$$R' = \text{primary};\ X = Br,\ I$$

tert-alkyl halides is not synthetically useful. In addition to this shortcoming, the use of the phosphine-coordinated reagent **2** suffers the considerable additional failing that product isolation is severely complicated by the presence of the residual tertiary phosphine. Several alternative procedures have been developed which diminish this undesirable quality. For example, Corey and Beames[4] replaced the trialkylphosphine with tris(dimethylamino)phosphine, $[(CH_3)_2N]_3P$, while Posner and coworkers[5] pioneered the development of an alternative class of mixed cuprates **4** prepared from the heterocopper species **3** (eq 3). However, these systems are not without

$$\underset{3}{Het\text{-}Cu} + RLi \rightarrow \underset{4}{(Het)(R)CuLi} \qquad (3)$$
$$Het = t\text{-}BuO,\ PhO,\ t\text{-}BuS,\ PhS,\ Et_2N$$

their own failings. Thus, tris(dimethylamino)phosphine, aside from being a costly agent, reacts violently with water[6] and the mixed heterocuprate **4**, although more stable than previous cuprate reagents, fails to produce significant yields of coupled product with a broad spectrum of alkyl substrates.[5] Finally, the successful application of phosphine-free reagents (prepared, as currently practiced, by the direct reaction of 2 equiv of primary alkyl-, vinyl-, or aryllithium reagents but not secondary or tertiary alkyllithium reagents with copper iodide) is limited to reaction with primary halides and tosylates (eq 4).[3c,7,8]

$$2RLi + CuI \rightarrow \text{“}R_2CuLi\text{”} \xrightarrow{R'X} R\text{-}R' \qquad (4)$$
$$R = \text{primary, vinyl, aryl};\ R' = \text{primary}$$

This paper reports the results of our investigation of the utility of polymer-bound triphenylphosphine–lithium organocuprates as synthetic reagents, as well as modifications in certain previously reported procedures which permit improved convenience and enhanced yields in coupling reactions involving secondary and tertiary alkylcopper reagents.

Results

Preparation and Characterization. Recent years have witnessed an increasing interest in the application of polymer-supported reagents in a diverse number of chemical transformations.[9-11] Several of these studies employed cross-linked polymeric triarylphosphines **5** as the base support. We have extended this concept to the

---

(1) Allied Chemical Fellow, 1978–1979.

(2) For recent reviews, see: (a) Posner, G. H. *Org. React.* **1972**, *19*, 1; **1975**, *22*, 253. (b) Normant, J. F. *Synthesis* **1972**, 63.

(3) (a) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. (b) House, H. O.; Fischer, W. F., Jr. *Ibid.* **1968**, *33*, 949. (c) Whitesides, G. M.; Fischer, W. F., Jr.; San Filippo, J., Jr.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

(4) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.

(5) Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.

(6) Mandeville, W. H.; Whitesides, G. M. *J. Org. Chem.* **1974**, *39*, 400.

(7) Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777.

(8) Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911; **1968**, *90*, 5615

(9) Demon, B.; James, G., Eds. "Catalysis: Heterogeneous and Homogeneous"; Elsevier: New York, 1975.

(10) Cf.: (a) Pitmann, C. U., Jr.; Smith, L. R.; Hanes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 1742. (b) Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J. *J. Catal.* **1976**, *43*, 322. (c) Pittman, C. U., Jr.; Evans, G. O. *CHEMTECH* **1973**, 560. (d) Ledwith, A.; Sherrington, D. C. In "Molecular Behavior and the Development of Polymeric Materials"; Wiley, New York, 1976; p 303. (e) Regan, S. L.; Lee, D. P. *J. Org. Chem.* **1975**, *40*, 1669.

(11) (a) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135 and references therein. (b) Reed, J.; Eisenberger, P.; Teo, B.-K.; Kincaid, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5217.

0022-3263/79/1944-2705$01.00/0

Table I. Dimer Yields Obtained on Oxidation of ⓅPh_2PCuR_2Li with Dioxygen and Nitrobenzene in THF at −78 °C[a]

R	oxidant	R-R,[b] %	comment
n-C_4H_9	O_2	48	yield of *n*-octane from the equivalent oxidation of $(n\text{-}C_4H_9)_2CuLiP(n\text{-}C_4H_9)_3$ is 84 and 90%, respectively[6,13]
	$PhNO_2$	51	
sec-C_4H_9	O_2	53	yield of 3,4-dimethylhexane from the equivalent oxidation of $(sec\text{-}C_4H_9)_2CuLiP(n\text{-}C_4H_9)_3$ is 82 and 80%, respectively[6]
	$PhNO_2$	53	

[a] Reaction mixtures were prepared by the addition of a solution of alkyllithium reagent (6.00 mmol) to a suspension of 6 (3.00 mmol based on copper assay) in THF at 0 °C. After the prescribed reaction period (see Experimental Section) the reagent mixture was cooled to −78 °C, the resulting mixture was compacted by centrifugation in a centrifuge bucket packed with dry ice, and the supernatant solution was transferred by cannula under a positive pressure of nitrogen to a flame-dried, nitrogen-flushed vessel and subsequently oxidized. [b] Yields are based on moles of alkyllithium added.

preparation of polymer-supported, triphenylphosphine–lithium dialkylcuprates 7 by the procedure outlined in Scheme I.

Scheme I. Preparation of Polymer-Bound Triphenylphosphine–Lithium Diorganocuprates[14]

$$\underset{5}{\text{Ⓟ}Ph_2P} \xrightarrow{(n\text{-}Bu_2S)_2CuI} \underset{6}{\text{Ⓟ}Ph_2P\cdot CuI} \qquad (5)$$

$$6 + 2RLi \rightarrow \underset{7}{\text{Ⓟ}Ph_2P\cdot CuR_2Li} + LiI \qquad (6)$$

The nature of the material designated as 7 is a matter of interest and several observations suggest its representation as a wholly polymer-bound reagent is inaccurate. Thus, a sample of 7 (R = n-C_4H_9, ~3.0 mmol) was compacted by centrifugation at −70 °C and the chilled supernatant solution was removed and replaced with fresh THF. This mixture was shaken vigorously and the entire process repeated two additional times. The resulting suspension of polymer was treated with 1.0 mmol of 1-bromooctane. Analysis of the subsequent product mixture indicated a 33% yield, *based on organic halide*, of *n*-dodecane. Addition of an equivalent amount of 1-bromooctane to the supernatant solution produced a 96% yield of *n*-dodecane.[26]

These results suggest that a significant fraction of the lithium di-*n*-butylcuprate present in the mixture designated as 7 is not polymer bound. It follows that copper–phosphine coordination in this reagent must be quite labile.[12] This conclusion is sustained by two additional observations.

First, oxidation[3c,6,13] of the isolated supernatant solution with either dioxygen or nitrobenzene resulted, respectively, in a 48 and 51% yield of *n*-octane. By comparison, similar oxidation of the residual suspension of polymer produced ≤1% yield of *n*-octane, while oxidation of 7 with either reagent prior to the removal of supernatant solution resulted in a 46% yield of *n*-octane (cf. Table I).

Second, when 6 was subjected to repeated extraction with THF similar to that described above for 7, elemental analysis indicated no significant alteration in its chemical composition. However, elemental analysis of the residual polymer produced by treating 7 in this manner revealed a 66% reduction in copper content.[15] Quantitative assay of the resulting supernatant solution revealed that essentially all of the missing copper was present in this phase.

The conclusion that significant copper–phosphine dissociation occurs in 7 raises the interesting question of what role such a process might play in the overall mechanism of cuprate coupling reactions involving the homogeneous reagent 2. Along these lines, Whitesides and Mandeville[6] observed that alkylation of certain mixed lithium diorganocuprates is substantially faster in the presence of 2 equiv of tri-*n*-butylphosphine than when no phosphine was employed. These workers also noted that the presence or absence of phosphine had a significant influence on the product distributions produced in some instances. The relationship between these observations is not clear; however, the results presented here do make one fact apparent: the previous perception of the role of the tertiary phosphines in these reagents as one of an essentially innocuous agent serving only to enhance the thermal stability of 2 may not be an accurate one.

Reaction with Alkyl Halides and Tosylates. Table II summarizes the results obtained from the reaction of 7 with a representative series of alkyl halides and tosylates. Although the methodology employed in these reactions is similar to that used for nonsupported reagents, several aspects of this procedure merit brief comment.

First, the formation of the active reagent required 15–30 min at 0 °C (R = n-C_4H_9, *sec*-C_4H_9, *t*-C_4H_9) or ambient temperatures (R = CH_3, C_6H_5). Second, the reactivity of this reagent parallels that of the homogeneous phosphine-coordinated reagent[3c] $R_2CuLi(PR'_3)$ with some noteworthy exceptions. Specifically, the successful coupling of a primary, secondary, or tertiary alkyl group with primary halides or tosylates, previously observed for the homogeneous reagent $R_2CuLi(PR'_3)$, can also be effected by 7 (eq 7) but without the major inconvenience that

$$\underset{7}{\text{Ⓟ}Ph_2PCuR_2Li} + R'X \xrightarrow{\geq 90\%} R\text{-}R' \qquad (7)$$

R = primary, secondary, tertiary; R′ = primary

accompanies product isolation in homogeneous systems. Moreover, the yield of coupling product in most instances is comparable to that obtained with an equivalent ho-

---

(12) The solution behavior of several halocopper(I)–tertiary phosphine complexes has been found to be quite complex: Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114.

(13) Whitesides, G. M.; San Filippo, J., Jr.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302.

(14) The structure designated as 6 is not meant to imply a particular geometry or ligand disposition but rather to reflect the elemental analysis of this material which indicates a strict 1:1:1 stoichiometry of phosphorus to copper to iodine. In light of the structural rearrangements and complexities that exist in tertiary phosphine–copper(I) halide complexes,[16] the actual structure of 6 is undoubtedly more complicated. Interestingly, it was observed that treatment of 5 with $(n\text{-}Bu_2S)_2CuI$ will not produce 6 with a high incorporation of copper(I) iodide unless the concentration of $(n\text{-}Bu_2S)_2CuI$ in the reaction mixture is ≤0.16 M. The origin of this behavior is not altogether clear but may be related to the concentration dependence on the degree of association of $(n\text{-}Bu_2S)_2CuI$ in solution.[16,19] Moreover, attempts to increase the copper content of polymers with a low copper(I) iodide incorporation (ca. 98% phosphorylated; Cu/P = 0.63) by further treatment with $(n\text{-}Bu_2S)_2CuI$ proved uniformly unsuccessful: analysis of recovered polymer indicated the copper content was essentially unchanged.[17]

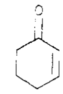
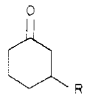
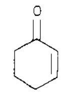
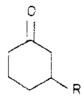
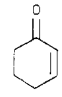
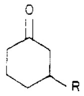
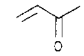
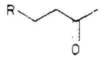
(15) Concomitant elemental analysis of the residual polymer for halide indicated 1 mol of iodide/mol of copper, suggesting that all the residual copper is, in fact, present as unreacted 6.

Table II. Yields of Coupled Product from the Reaction of ⓅPh$_2$PCuR$_2$Li (7) with Octyl Halides and Tosylates[a]

R	R'X	reacn conditions[b]	R-R',[c] %
CH_3	n-$C_8H_{17}Cl$	I	97
	n-$C_8H_{17}Br$	II	99
	n-$C_8H_{17}I$	II	98
	sec-$C_8H_{17}Cl$	I	2
	sec-$C_8H_{17}Br$	II	82
	sec-$C_8H_{17}I$	II	95
n-C_4H_9	n-$C_8H_{17}Cl$	III	79
	n-$C_8H_{17}Br$	IV	99
	n-$C_8H_{17}I$	IV	65 (75)[d]
	n-$C_8H_{17}Cl$	III	63[e]
	n-$C_8H_{17}Br$	IV	55[e]
	n-$C_8H_{17}I$	IV	28[e]
n-C_4H_9	sec-$C_8H_{17}Cl$	V	2
	sec-$C_8H_{17}Br$	VI	1 (22)[f]
	sec-$C_8H_{17}I$	VI	56 (61)[f]
	sec-$C_8H_{17}OTs$	VI	56
sec-C_4H_9	n-$C_8H_{17}Cl$	VI	7
	n-$C_8H_{17}Br$	VI	79 (89)[d]
	n-$C_8H_{17}I$	VI	81 (86)[d]
	n-$C_8H_{17}OTs$	VI	68 (84)[e]
t-C_4H_9	n-$C_8H_{17}Cl$	VI	68
	n-$C_8H_{17}Br$	VI	97
	n-$C_8H_{17}I$	VI	99
	n-$C_8H_{17}OTs$	VI	97
C_6H_5	n-$C_8H_{17}Cl$	I	23
	n-$C_8H_{17}Br$	II	71
	n-$C_8H_{17}I$	II	73
	sec-$C_8H_{17}Cl$	I	0
	sec-$C_8H_{17}Br$	II	0
	sec-$C_8H_{17}I$	II	0

[a] All reactions were carried out in THF by using 3.5 mmol of **6** (based on copper assay) and 6.0 mmol of alkyllithium unless noted otherwise. Coupled product yields are significantly affected by the reaction conditions employed in the preparation of **7** as well by the conditions employed during the coupling reaction (see text). The yields given here have been optimized with these factors in mind. [b] I, reaction mixtures were stirred for 30 min at ambient temperature followed by 3 h at reflux; II, reaction mixtures were stirred for 30 min at room temperature followed by 2 h at reflux; III, reaction mixtures were stirred for 30 min at −78 °C, followed by 30 min at 0 °C, followed by 5 h at ambient temperature; IV, reaction mixtures were stirred for 1 h at −78 °C and subsequently allowed to warm to room temperature over a period of 1 h; V, reaction mixtures were stirred for 1 h at −78 °C, followed by 4 h at 0 °C, followed 17 h at ambient temperature; VI, reaction mixtures were stirred for 1 h at −78 °C, then permitted to warm to room temperature over a period of 1 h, and finally stirred at ambient temperature for an additional 2 h. [c] Yields were determined by GLPC and are based on starting halide or tosylate. [d] Mixtures treated in this manner were not permitted to warm to room temperature but instead were stirred for 1 h at −78 °C and then for an additional 1 h at −15 °C before oxidation with an excess of nitrobenzene at −78 °C. [e] Reactions carried out in diethyl ether. [f] These yields were obtained by using samples of complex **6** that had undergone extended reaction with iodo[bis(di-n-butyl sulfide)copper(I)]. Elemental analysis of this material indicated a molar ratio of Cu to P of 1.16 (see text).

Table III. Yields of Conjugate Adducts from the Reaction of ⓅPh$_2$PCuR$_2$Li[a] (7) with 2-Cyclohexenone and Methyl Vinyl Ketone

R	enone	reacn conditions[b]	product (%)[c]
CH_3		I	 (83)
n-C_4H_9		II	 (63)
t-C_4H_9		II	 (87)
n-C_4H_9		II	 (72)

[a] Generated by the reaction of 6.0 mmol of alkyllithium with 3.5 mmol (based on copper assay) of complex **6** suspended in THF. [b] Time and temperature: I, 3 h, ambient; II, after 1 h at −78 °C, the reaction mixture was permitted to warm to ambient temperature over a 1-h period and to remain for 2 h at this temperature. [c] Yields were determined by GLPC and are based on starting enone.

mogeneous reagent. Third, solvent effects are in keeping with those previously noted.[3c,7] Finally, oxidation of several reaction mixtures prior to hydrolysis increased (in some instances substantially) the yield of coupled product. This fact strongly suggests[3c] that metal–halogen exchange has taken place. Since such reactivity is not characteristic of lithium diorganocuprates,[3c] it follows that the reagent designated as **7** contains some free organolithium reagent.

The degree of polymer loading has been noted to influence the nature of polymer-supported reagents.[11] In an effort to determine what effect this parameter might have on the reactivity of reagent **7**, we have examined the alkylation of a representative series of n-octyl halides with **7** (R = n-C_4H_9), prepared from polymers with different degrees of copper incorporation. The results, summarized in Table V, reveal that a generally monotonic decrease occurs in coupling efficiency as the degree of loading is reduced.[17] Optimum yields were obtained by using a polymer with maximum incorporation of copper.

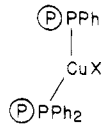
Reaction of 7 with α,β-Unsaturated Ketones. The utility of lithium organocuprates in effecting conjugate addition of alkyl, aryl, and vinyl groups to α,β-unsaturated substrates has been amply demonstrated.[2,3a,18] We have examined the reactions of **7** with several α,β-unsaturated ketones in order to determine the reactivity of this reagent under these circumstances. The results of these experiments are summarized in Table III. Yields, based on starting ketone, of conjugate adduct are, in general, comparable to those obtained with equivalent homogeneous reagents.

Preparation and Reactions of Nonpolymer-Supported Organocopper(I) Reagents. The direct reaction of organolithium reagents with copper iodide produces organometallic solutions, the composition of

---

[16] Cf.: Churchill, M. R.; and Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899 and references therein.

[17] A reasonable explanation of this effect is that it follows from the formation of polymer-bound, ligand-bridged species such as **9**, which results



9

from site–site interactions. Such interactions are favored in lightly cross-linked (and, therefore, relatively mobile) polymer matrices having a high degree of functionalization (phosphorylation) and low coverage (metal loading).[11]

[18] House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. House, H. O.; Umen, M. J. *Ibid.* **1973**, *38*, 3893.

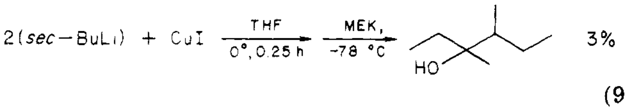
which is not well defined.[3c,20] Still, preparations of this nature are most amenable to large-scale synthetic application and this procedure is much used for this purpose. However, this method as currently practiced has certain limitations; specifically, the utility of this procedure in effecting coupling reactions involving alkyl halides and tosylates is largely limited to the coupling of primary alkyl-, vinyl-, and aryllithium reagents with these substrates according to eq 8.[3c,7,8]

$$2\mathrm{RLi} + \mathrm{CuI} \xrightarrow{\mathrm{THF}} \underset{\mathbf{8}}{\text{“}\mathrm{R_2CuLi}\text{”}} \xrightarrow{\mathrm{R'X}} \mathrm{R{-}R'} \qquad (8)$$

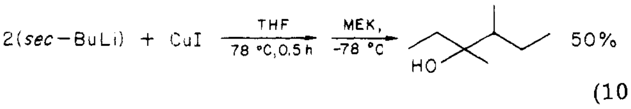
$$\mathrm{R} = \text{primary, vinyl, aryl; } \mathrm{R'} = \text{primary}$$

Consistent with previous studies,[3c,8] we observed that the reagent produced by the reaction of *tert*-butyl- or *sec*-butyllithium with copper iodide in THF at -78 °C does not couple to any appreciable extent with alkyl halides (cf. Table VI). However, we have further observed that the reagent prepared at 0 °C *does* couple with alkyl halides in good to excellent yields. These results are summarized in Table IV.

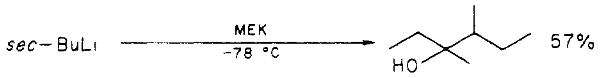
Such data suggest that in these and presumably analogous instances the formation of the active organocopper reagent 8 occurs readily at 0 °C but not at -78 °C.[21] In an effort to substantiate this contention we have examined the reaction of one such reagent mixture, prepared at two different temperatures, with methyl ethyl ketone (MEK).[22] The results of this study, presented in eq 9–11, are clearly



(9)



(10)



(11)

consistent with this interprepation and emphasize the importance of carrying out the preparation of 8 at a relatively elevated temperature rather than at the lower temperatures as previously preferred. The influence is illustrated by a further comparison.

Table IV. Yield of Coupled Product Produced by Alkylation of the Mixture Generated by Addition of n-C_4H_9Li, sec-C_4H_9Li, or $tert$-C_4H_9Li to Copper(I) Iodide at 0 °C[a]

$$2\mathrm{RLi} + \mathrm{CuI} \xrightarrow[0\ ^\circ\mathrm{C},\ \mathbf{8}]{\mathrm{THF}} \xrightarrow[-78\ ^\circ\mathrm{C},\ 1\ \mathrm{h}]{\mathrm{R'X}} \xrightarrow[3\ \mathrm{h}]{25\ ^\circ\mathrm{C}} \mathrm{R{-}R'}$$

RLi	amt of CuI, mmol	R'X	R-R',[b] %
t-C_4H_9Li	3.0	n-$C_8H_{17}I$	92
	3.0	n-$C_8H_{17}Br$	93
	3.0	n-$C_8H_{17}Cl$	89
	3.0	n-$C_8H_{17}OTs$	84
	3.0	sec-$C_8H_{17}I$	12
sec-C_4H_9Li	3.0	n-$C_8H_{17}I$	72 (86)[c]
	3.0	n-$C_8H_{17}Br$	77 (87)[c]
	3.0	n-$C_8H_{17}Cl$	60
	3.0	n-$C_8H_{17}OTs$	72 (78)[d]
	3.0	sec-$C_8H_{17}I$	25
	3.0	sec-$C_8H_{17}OTs$	23 (32)[d]
n-C_4H_9Li	3.0	n-$C_8H_{17}Cl$	93
	3.0	n-$C_8H_{17}Br$	93 (97)[c]
	3.0	n-$C_8H_{17}I$	46 (77)[c]
	3.0	n-$C_8H_{17}OTs$	86 (88)[d]

[a] Unless otherwise noted the alkyl halide or tosylate (1.00 mmol) was added to 8 at -78 °C; the resulting mixture was stirred for 1 h at -78 °C and then for 3 h at 25 °C before workup. [b] Yields were determined by GLPC and are based on starting halide or tosylate. [c] Mixtures treated in this manner were not permitted to warm to room temperature but instead were stirred for 1 h at -78 °C and then for an additional 1 h at -15 °C before oxidation with an excess of nitrobenzene at -78 °C. [d] Reactions were carried out in diethyl ether.

Table V. Effect of Polymer Loading on the Yield of Coupled Product R-R' from Reaction of ⓅPh_2PCuR_2Li with 1-$C_8H_{17}X$ in THF[a]

R	X	loading,[b] %	reacn conditions[c]	n-$C_{12}H_{26}$,[d] %
n-C_4H_9	I	98	I	65
	Br	98	I	99
	Cl	98	II	78
n-C_4H_9	I	73	I	56
	Br	73	I	93
	Cl	73	II	52
n-C_4H_9	I	63	I	39
	Br	63	I	75
	Cl	63	II	41

[a] All reactions employed 3.5 mmol of 6 (calculated on the basis of copper content) and 6.0 mmol of n-butyllithium. [b] Samples of 6 with a copper loading of <100% (i.e., polymer for which elemental analysis indicated a Cu:P ratio less than that calculated for ⓅPh_2PCuI) were prepared by treating samples of 5 (for which analysis indicated a phosphorus content >98% of that calculated for ⓅPh_2P) with a quantity of $[(n\text{-}C_4H_9)_2S]_2CuI$ as described in the Experimental Section. [c] Time and temperature: I, after 1 h at -78 °C, the reaction mixture was permitted to warm to ambient temperature over a 1-h period; II, after 0.5 h at -78 °C, the reaction mixture was placed in an ice bath for 0.5 h and finally allowed to remain for 5 h at ambient temperature. [d] Yields were determined by GLPC and are based on starting halide.

It is clear from Table VI that the success of the coupling reaction involving 8 depends significantly upon the conditions under which the reagent 8 is prepared: both the solvent and temperature of this reaction play an important role in determining the formation *and* subsequent stability of 8. For example, the relative stability of 8 (R = t-C_4H_9) prepared in THF at 0 °C contrasts sharply with the equivalent preparation in ether under similar conditions. Indeed, there are even substantial visual differences in the appearances of the two reagents: the former appears as deep burgandy colored solution while the latter occurs as a suspension of black particulates in a colorless mother liquor. Moreover, as the preparation temperature of 8 in ether is lowered from 0 to -40 °C, the physical appearance of the resulting mixture approaches that observed for the equivalent preparation in THF at 0 °C. It follows that any attempt to correlate reactivity patterns adduced from the efficiency of coupled product formation must take care to ensure that the apparent reactivity of such reagents is not in fact a reflection of reagent instability or incomplete

---

(19) San Filippo, J., Jr.; Zyontz, L. E.; Potenza, J. *Inorg. Chem.* **1975**, *14*, 1667.

(20) San Filippo, J., Jr. *Inorg. Chem.* **1978**, *17*, 275.

(21) A related observation has been made by others: House, H. O.; and DuBose, J. C. *J. Org. Chem.* **1975**, *40*, 788 (cf. ref 2(a) and 7).

(22) Lithium diorganocuprates do *not* react with simple ketones. For example

$$(\mathrm{CH_3})_2\mathrm{CuLi} + \mathrm{C_6H_6C(O)CH_3} \xrightarrow[0\ ^\circ\mathrm{C},\ 24\ \mathrm{h}]{\mathrm{Et_2O}} \xrightarrow{\mathrm{H_3O^+}} \underset{7\%}{\mathrm{C_6H_5CHOHCH_3}}$$

Table VI

$$2RLi + CuI \xrightarrow{A} \xrightarrow[R'X]{B} \xrightarrow{C} R\text{-}R'$$

R	R'X	reaction conditions	A	B	C	yield of R-R', %
t-BuLi	n-$C_8H_{17}OTs$	solvent	THF	THF	THF	84
		temp, °C	0	−78	25	
		time, h	0.25	1.0	3.0	
t-BuLi	n-$C_8H_{17}OTs$	solvent	THF	THF	THF	88
		temp, °C	0	−78	25	
		time h	1.0	1.0	3.0	
t-BuLi	n-$C_8H_{17}OTs$	solvent	Et_2O	Et_2O	Et_2O	17
		temp, °C	0	−78	25	
		time, h	0.25	1.0	3.0	
t-BuLi	n-$C_8H_{17}OTs$	solvent	Et_2O	Et_2O	Et_2O	12
		temp, °C	0	−78	25	
		time, h	0.5	1.0	2.0	
t-BuLi	n-$C_8H_{17}OTs$	solvent	Et_2O	Et_2O	Et_2O	85
		temp, °C	−40	−78	25	
		time, h	0.5	1.0	3.0	
t-BuLi	n-$C_8H_{17}I$	solvent	THF	THF	THF	98
		temp, °C	0	−78	25	
		time, h	1.0	1.0	3.0	
t-BuLi	n-$C_8H_{17}I$	solvent	THF	THF	THF	3
		temp, °C	−78	−78	25	
		time, h	0.50	1.0	2.0	
sec-BuLi	n-$C_8H_{17}Br$	solvent	THF	THF	THF	20
		temp, °C	−78	−78	25	
		time, h	0.5	1.0	2.0	
sec-BuLi	n-$C_8H_{17}Br$	solvent	THF	THF	THF	87
		temp, °C	−78	−78	25	
		time, h	0.50	1.0	2.0	

formation resulting from undetermined temperature and/or solvent effects.

Perhaps most surprising is the comparative stability of 8 (R = t-C_4H_9) and lithium di-*tert*-butyl(tri-*n*-butylphosphine)cuprate. The former reagent shows little decomposition in THF after 1 h at 0 °C while the latter complex undergoes essentially complete decomposition after 20 min under comparable conditions.[3c]

Finally, it was observed that oxidation with either dioxygen or nitrobenzene of mixtures produced by the reaction of 8 with alkyl halides, like those involving the similar reaction of 7, produced increased yields of coupled product. We conclude that some metal–halogen exchange, attributable to the presence of free alkyllithium reagent, is occurring in these mixtures.

Discussion

The reaction of organolithium reagents with polymer-bound triphenylphosphinecopper(I) iodide produces a reagent mixture whose reactivity in alkylation and conjugate addition is generally comparable or superior to that of the related homogeneous reagent 2, prepared by the analogous reaction with tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] or an equivalent complex. It is apparent, however, that the alkylating agent in this mixture is, to a substantial degree, not polymer bound. Rather, the polymer serves in this instance as an agent for the efficacious introduction and removal of, respectively, copper(I) iodide and triphenylphosphine.

From the perspective of synthetic utility the necessity for employing tertiary phosphine complexes of copper(I) halides in the preparation of lithium diorganocuprates has rested on the recognition of the fact that these precursors provide the essentially exclusive means by which the successful coupling of a complete spectrum (R = primary, secondary, tertiary, aryl, vinyl) of lithium diorganocuprates with alkyl halides and tosylates can be achieved—a scope unmatched by other procedures which, however, can be useful for less general preparations. This necessity, however, would seem to have been obviated by the observation that the reagent produced by the direct reaction of *sec*- or *tert*-butyllithium with a suspension of copper(I) iodide in THF at 0 °C is capable of effecting efficient coupling with alkyl halides and tosylates. Since the equivalent reaction of primary alkyl-, vinyl-, and aryllithium reagents is already established as providing reagent mixtures capable of moderate to excellent coupling efficiency, it would appear that, with proper attention to reaction temperature and solvent, the enhanced scope afforded by the phosphine-coordinated reagent 2 can also be achieved with phosphine-free reagents prepared by the direct reaction of an organolithium reagent with a suspension of copper(I) iodide.

Experimental Section

General Methods. Tetrahydrofuran and diethyl ether were purified by distillation from lithium aluminum hydride under an atmosphere of prepurified nitrogen. All solvents and solutions of organometallic reagents were transferred by using hypodermic syringes or stainless steel cannulas under inert atmospheres of dry, prepurified nitrogen or helium. Methyl vinyl ketone and 2-cyclohexen-1-one were distilled immediately prior to use.

Solutions of *n*-butyllithium in hexane and phenyllithium in benzene–ether (70:30) were obtained from Alfa Inorganics. Solutions of *sec*-butyllithium in hexane and *tert*-butyllithium in pentane were purchased from Aldrich Chemical Co. Methyllithium in ether was obtained from Lithium Corp. of America. Organolithium reagents were assayed by using the Gilman double-titration procedure. Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] was prepared by the literature procedure.[23] Authentic samples of the products octane, nonane, dodecane, 1-phenyloctane, 2-methyloctane, 3,4-dimethylhexane, 3,4-dimethyl-3-hexanol, 2-octanone, and 3-methylcyclohexanone were obtained from the Aldrich Chemical Co. or Chemical Samples Co. Others were prepared as described below.

---

[23] Kaufman, G. B.; and Teter, L. A. *Inorg. Synth.* **1963**, 7, 9.

Product mixtures were analyzed by GLPC by using internal standard techniques. All products were identified by comparison of their retention times with those of an authentic sample as well as by comparison of mass spectra. Peak areas were obtained with the aid of a Hewlett-Packard Model 3380A electronic integrator.

Polystyrene beads (1–2% cross-linked with divinylbenzene) were purchased from Bio-Rad Laboratories and pretreated according to the procedure described by Relles.[24] Chlorodiphenylphosphine was purchased from the Aldrich Chemical Co. and distilled prior to use. 1-Octyl tosylate and 2-octyl tosylate were prepared according to the procedure of Streitweiser.[25] 2-Iodo-, 2-bromo-, and 1-iodooctane were purchased from Eastman and purified by chromatography through a short column of activated alumina prior to use.

Analytical GLPC analyses were carried out on either a Hewlett-Packard Model 5750 or Varian 1400 gas chromatograph equipped with flame ionization detectors. Preparative GLPC was performed on a Varian Model 90-P instrument. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-7 mass spectrometer. ^{1}H NMR were recorded on a Varian Model T-60 spectrometer; chemical shifts are reported in parts per million relative to internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 727B grating spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Copper iodide was purchased from Fischer Scientific Co. and used without further purification. Iodo[bis(di-*n*-butyl sulfide)copper(I)] was prepared according to the literature procedure.[19]

2,2-Dimethyldecane. Into a flame-dried, three-necked, 100-mL flask equipped with a Teflon-coated stirring bar was placed 10.04 g (6.39 mmol) of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)]. The flask was stoppered with rubber septums and the contents were flushed with nitrogen before adding 50 mL of THF through a cannula. The resulting solution was cooled to −78 °C and a solution of *tert*-butyllithium (33.0 mL, 51.5 mmol) was added by syringe. This solution was stirred at −78 °C for 20 min before adding 1.054 g (5.40 mmol) of 1-bromooctane. The subsequent mixture was stirred at −78 °C for 20 min and then allowed to warm and stir at room temperature for 10 h before hydrolyzing with 50 mL of 3 M HCl. The resulting mixture was passed through a short (6 in.) column of alumina, and the eluent was collected and extracted with a saturated aqueous solution of NH_4Cl, followed by a saturated aqueous solution of $NaHCO_3$, and finally dried ($MgSO_4$) and concentrated.

The residual oil was subjected to bulb-to-bulb distillation (11 torr) by using a heat gun: yield 0.713 g (77%) of a colorless liquid (96% pure by GLPC); IR (neat) 2929, 1468, 1398, 1363, 1250 cm^{-1}; MS *m/e* (relative intensity at 30 ev) 170, 85 (6.8), 71 (9.8), 57 (100), 56 (55), 43 (10), 41 (6.0).

3-Methylundecane. A procedure similar to that described above was used employing 8.6 mL (12.0 mmol) of a solution of *sec*-butyllithium, 2.70 g (1.72 mmol) of $[CuI\cdot P(n\text{-}C_4H_9)_3]_4$, and 0.4214 g (2.182 mmol) of 1-bromooctane. The yield of 3-methylundecane was 76%. The final product was purified by preparative GLPC: IR (neat) 2975, 2940, 2885, 1470, 1388 cm^{-1}; MS *m/e* (relative intensity) 170 (just visible), 141 (9.6), 140 (8.8), 99 (8.8), 85 (37), 71 (45), 57 (100), 56 (34), 55 (7.2), 43 (18), 41 (9.2).

5-Methylundecane. Into a flame-dried, three-necked, 50-mL flask equipped with a Teflon-coated stirring bar and a reflux condenser and capped with rubber septums was placed ether (20 mL) followed by 10.5 mL (25.9 mmol) of *n*-butyllithium. The mixture was cooled in an ice bath, and 2-octanone (1.61 g, 12.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 12 h and then hydrolyzed by the cautious addition of 3 N HCl (10 mL). The layers were separated and the aqueous phase was extracted with two 20-mL portions of ether. The combined organic phases were dried ($MgSO_4$) and concentrated to yield 1.99 g of a light yellow liquid found by GLPC to be 81% (69% yield) 5-methyl-5-undecanol: IR (film) 3375, 2925, 2860, 1715 (2-octanone impurity), 1473, 1380, 1160 cm^{-1}. This product was used without further purification.

A mixture of 5-methyl-5-undecanol (1.99 g, 10.70 mmol), 17 mL of pyridine, and 8.00 g (52.0 mmol) of $POCl_3$ was stirred at room temperature for 23 h and then poured into a separatory funnel containing crushed ice overlaid with pentane. The layers were separated and the aqueous phase was extracted with two 15-mL portions of pentane. The combined organic phases were washed with 3 N HCl (80 mL) and then with saturated $NaHCO_3$, dried ($MgSO_4$), concentrated, and subjected to bulb-to-bulb distillation to give 1.29 g of a mixture of isomeric olefins: IR (film) 2967, 2927, 2852, 1717, 1462, 1377, 1163, 892 cm^{-1}; NMR (CCl_4) δ 5.08 (crude triplet, $J \approx 7$ Hz, trisubstituted olefin), 4.65 (crude singlet, *gem*-disubstituted olefin), 2.50–1.72 (allylic hydrogens, complex), 1.72–0.63 (aliphatic hydrogens, complex).

This mixture of olefins (1.00 g) was hydrogenated over PtO_2 in glacial acetic acid (17 mL). The resulting product mixture was filtered into a separatory funnel containing water overlaid with pentane. The layers were separated and the organic phase was washed with water and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), concentrated, and distilled (bulb-to-bulb, 3 torr), giving 1.036 g of a colorless liquid which GLPC analysis indicated to be 95% 5-methylundecane. An authentic sample of the product was obtained by preparative GLPC: IR (film) 2952, 2922, 2862, 1470, 1380, 1262, 1102, 1022, 807, 730 cm^{-1}; MS *m/e* (relative intensity) 170 (2.3, M$^+$), 113 (11), 112 (22), 85 (50), 84 (40), 71 (70), 70 (11), 69 (15), 57 (100), 56 (25), 55 (22), 44 (49).

3-*n*-Butylcyclohexanone. Into a flame-dried, three-necked, 100-mL flask equipped with a Teflon-coated stirring bar and a reflux condenser and capped with rubber septums was placed 2.86 g (15.0 mmol) of copper(I) iodide followed by 25 mL of THF. The suspension was cooled (ice bath) and *n*-butyllithium (12.5 mL, 30.0 mmol) was added by syringe. The deep burgundy solution was stirred at 0 °C for 15 min before adding freshly distilled 2-cyclohexen-1-one (490 mg, 5.09 mmol) dropwise. This mixture was stirred at 0 °C for 3 h followed by an additional 3 h of stirring at room temperature and then hydrolyzed with 40 mL of aqueous ammonium chloride. After 1 h of stirring, this mixture was filtered through a column of alumina and extracted with ether; the organic extract was washed with 3 N HCl and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated, giving 1.044 g of a pale yellow liquid found to be 56% 3-*n*-butylcyclohexanone (75% yield) by GLPC. The product was purified by preparative GLPC: IR (film) 2925, 2850, 1708, 1453, 1427, 1350, 1320, 1230, 1127, 1060, 878 cm^{-1}; MS *m/e* (relative intensity) 154 (6.4), 111 (25), 99 (13), 98 (100), 83 (9), 69 (18), 68 (8), 56 (25), 55 (57), 43 (13), 42 (16), 41 (49).

Preparation of 3-*tert*-Butylcyclohexanone. A 300-cm^3 autoclave (Autoclave Engineers) was charged with catalyst (0.183 g, 5% Pd/C), 3-*tert*-butylphenol (58.4 g, 0.389 mmol), and 95% ethanol (8.0 mL). The vessel was sealed and flushed with hydrogen before heating to 160 °C, with stirring, under a hydrogen pressure of 500 psi. The course of the reaction was monitored at intervals. When the yield of 3-*tert*-butylcyclohexanone reached 30%, the corresponding yield of 3-*tert*-butylcyclohexanol was 1%. If the reaction was permitted to proceed further, the ratio of ketone to alcohol became less favorable; thus, the reaction was discontinued at this point. This product mixture was poured in petroleum ether (bp 30–60°) and extracted with 3 M NaOH to remove the unreacted phenol and then dried ($MgSO_4$) and concentrated under vacuum. Analysis of the crude product mixture on a 10-ft, 15% Carbowax column revealed a mixture consisting of 95% 3-*tert*-butylcyclohexanone and ~3% 3-*tert*-butylcyclohexanol; an authentic sample of the product was obtained by preparative GLPC: IR (film) 2950, 2870, 1710, 1482, 1375, 1248, 1230, 1180 cm^{-1}; NMR (CCl_4) δ 2.32–0.98 (9 H, complex multiplet), 0.62 (9 H, s); MS *m/e* (relative intensity) 154 (19), 99 (17), 98 (87), 97 (24), 83 (22), 70 (17), 69 (27), 57 (100), 55 (24), 41 (60).

Bromination of 1–2% Cross-Linked Polystyrene Beads. The following modification of a procedure previously reported by Relles and Schluenz[24] was found to give higher bromine incorporation.

---

[24] Relles, H. M.; Schluenz, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 6469.

[25] Streitweiser, A., Jr.; Walsh, T. D.; Wolfe, J. R., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3682.

[26] The yield of coupled product is calculated based on the millimoles of RX added to each mixture and not on the millimoles of copper present. Under such conditions the *combined* yield of coupled product may exceed 100% since the combined theoretical yield under such conditions is 200%.

Polystyrene (81.5 g, 0.783 mol of repeating unit, Bio-Rad 2 X-1) was suspended in 500 mL of nitromethane contained in a three-necked, 1-L flask. This flask was equipped with an overhead stirrer, a thermometer, and a Claisen-head adapter to which a 250-mL addition funnel was attached. The remaining neck was stoppered with a drying tube containing Drierite and used as a vent for gas expelled during the course of the reaction. The reaction vessel was wrapped in aluminum foil before placing it in an ice bath. The contents of the flask were saturated with BF_3 gas (50 g) at 0 °C. **Caution**! This and subsequent steps should be performed in a properly ventillated fume hood. Bromine (256 g, 1.60 mol) was added accompanied by efficient stirring and cooling over a 1-h period. During this time, the reaction temperature rose and remained between 10 and 18 °C. Reaction was accompanied by the copious evolution of gases which were partially trapped by passing the effluent through a concentrated aqueous solution of NaOH. With addition completed, the resulting reaction mixture was stirred at room temperature for an additional 12 h. The product was collected by suction filtration and washed first with one 500-mL portion of CH_2Cl_2, then with 500-mL portions of, respectively, 9:1, 3:1, 2:3, 3:1, and 9:1 CH_2Cl_2–CH_3OH, and then finally with pure CH_2Cl_2. The resulting material was dried at ambient temperature under a reduced pressure (20 torr) for 2–3 h on a rotary evaporator and subsequently at 100 °C (0.1 torr) for 3 h; yield 134.5 g. Anal. Calcd for C_8H_7Br: C, 52.46; H, 4.16; Br, 43.7. Found: C, 52.24; H, 4.24; Br, 43.5, corresponding to 99.5% bromine incorporation.

Treatment of brominated polystyrene with lithium diphenylphosphide was carried out by using a slightly modified version of the literature procedure.[24] Into a flame-dried, nitrogen-flushed, three-necked, 500-mL flask equipped with a Teflon-coated stirring bar and a 100-mL addition funnel and capped with rubber septums were placed pieces of lithium wire (ca. $^1/_8$ in., 6.4 g, 0.92 g-atom) followed by 250 mL of THF. The mixture was cooled to ca. 15 °C and chlorodiphenylphosphine (88.0 g, 0.440 mmol) was added dropwise over a period of 1 h. Following the addition, the deep red solution of lithium diphenylphosphide was allowed to stir at ambient temperature for an additional 4 h before it was transferred by cannula under a positive pressure of nitrogen to a stirred suspension of 4 (30.0 g, 0.164 mmol as repeating unit) in THF (200 mL) contained in a 1-L, three-necked, flame-dried flask equipped with a Teflon-coated stirring bar and a reflux condenser. Following the completed addition, the resulting mixture was refluxed with stirring for 4 h and then poured into anhydrous methanol (500 mL). This mixture was stirred for 30 min before the solid was collected by suction filtration. This material was washed successively with two 250-mL portions of anhydrous methanol, with 250-mL portions of 2:3, 3:1, and 9:1 (v/v) CH_2Cl_2–CH_3OH, and finally with pure CH_2Cl_2. The resulting solid was dried overnight at ca. 20 torr and then at 100 °C (1.0 torr) for 2 h. The final product, **5**, is a pale yellow solid (36.46 g). Anal. Calcd for $C_{20}H_{17}P$: P, 10.76. Found: P, 10.65.

Reaction of ⓅPh$_2$P with $[(n\text{-}C_4H_9)_2S]_2CuI$. Preparation of ⓅPh$_2$PCuI (**6**). Into a 1-L, three-necked flask equipped with a Teflon-coated stirring bar and reflux condenser was placed 16.09 g (54.8 mmol, calculated on a repeating unit basis) of **5** and 500 mL of toluene. The mixture was stirred for 0.5 h to effect swelling of the polymer. Iodo[bis(di-*n*-butyl sulfide)copper(I)] (35.32 g, 0.0732 mmol) was added and the resulting mixture was stirred for 11 h at room temperature after which it was refluxed for an additional 12 h. This solid was collected by suction filtration, washed with four 250-mL portions of toluene, and dried for 30 min on a rotary evaporator at 50 °C (20 torr) before a final drying at 100 °C (0.8 torr) for 2 h to yield 26.35 g of the pale yellow solid **6**. Anal. Calcd for $C_{20}H_{17}CuIP$: I, 26.45. Found: I, 26.17, corresponding to a 98% incorporation of copper(I) iodide.

The preparation of 6 with reduced copper iodide loading was effected by using *higher*[12] concentrations of iodo[bis(di-*n*-butyl sulfide)copper(I)] than described in the above procedure. The following example is representative. Polystyrene-supported triphenylphosphine (**5**, 29.0 g, 0.098 mol calculated on a repeating unit basis) was suspended in toluene (300 mL) and treated with iodo[bis(di-*n*-butyl sulfide)copper(I)] (48.2 g, 0.100 mol, 0.33 M) as described above. Analysis of the resulting product revealed a Cu:P ratio of 0.73, based on the phosphorus content (98%) of reagent **5**. The preparation of **6** with a Cu:P ratio of 0.63 was accomplished in a similar fashion by using a 0.88 M solution of iodo[bis(di-*n*-butyl sulfide)copper(I)] in toluene.

Preparation and Reaction of 7 with Alkyl Halides. R = Methyl and Phenyl (Typical Procedure). The precursor **6** (1.72 g, 3.50 mmol) was placed in a flame-dried, three-necked, 100-mL flask equipped with a Teflon-coated stirring bar and a reflux condenser. The contents of the flask were flushed with nitrogen before a volume of THF (25 mL) and a weighed amount of internal standard were added by syringe. The resulting mixture was stirred for 30 min before a solution of methyllithium or phenyllithium (6.00 mmol) was added by syringe. This mixture was allowed to stir at ambient temperature for an additional 30 min before 0.191 g (1.00 mmol) of *n*-octyl bromide was added by syringe. The resulting mixture was stirred at room temperature for 30 min and then heated at reflux for 2 h. This reaction mixture was cooled to room temperature and an aliquot (ca. 2–3 mL) was removed and treated with 0.2 mL of distilled water. The residual solids were compacted by centrifugation and the supernatant solution was analyzed by GLPC.

R = *sec*-Butyl (Typical Procedure). A weighed amount of the precursor **6** (1.72 g, 3.50 mmol) was placed in a flame-dried, three-necked, 100-mL flask equipped with a Teflon-coated stirring bar and reflux condenser. All remaining necks were stoppered with rubber septums and the contents of the flask were flushed with nitrogen. Tetrahydrofuran (25 mL) was added by syringe along with a known amount of internal standard. The contents of the flask were stirred for 30 min at ambient temperature and then chilled to 0 °C in an ice bath before a solution of *sec*-butyllithium was added by syringe. The resulting dark suspension was stirred at 0 °C for 30 min and then cooled to −78 °C before 0.240 g (1.00 mmol) of 1-iodooctane was added by syringe. The subsequent mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature and stir at this temperature for an additional 2 h before a workup similar to that described above was carried out.

R = *tert*-Butyl (Typical Procedure). The above procedure, slightly modified to accommodate the decreased stability of the organocopper reagent, was employed. Thus, the mixture resulting from the addition of a solution of *tert*-butyllithium (6.00 mmol, 3.85 mL) to a suspension of **6** (3.50 mmol, based on copper assay) in THF at 0 °C was stirred for 15 min before it was chilled to −78 °C and subsequently treated with 1-iodooctane (0.2401 g, 1.00 mmol).

R = *n*-Butyl (Typical Procedure). A procedure similar to that described above was employed. The mixture produced by the addition of a solution of *n*-butyllithium (6.00 mmol, 3.50 mL) to a suspension of **6** (3.50 mmol, based on copper assay) in THF at 0 °C was stirred at 0 °C for 30 min and then chilled to −78 °C before the appropriate amount of alkyl halide or tosylate (RX) was added. The subsequent mixture was stirred at −78 °C for 1 h (X = Br, I, OTs) and then allowed to warm to ambient temperature, with stirring, for an additional 1-h period. For alkyl chlorides (X = Cl) the reaction time included 0.5 h at −78 °C followed by 0.5 h at 0 °C and finally 5.0 h of stirring at ambient temperature.

Alkylation with *sec*-Butyl- and *tert*-Butyllithium–Copper(I) Iodide Mixtures. R = *n*-Butyl and R = *sec*-Butyl (Typical Procedure). Copper(I) iodide (0.517 g, 3.00 mmol) was placed in a flame-dried, three-necked, 100-mL flask equipped with a Teflon-coated stirring bar and reflux condenser. All openings were stoppered with rubber septums and the vessel and its contents were flushed with nitrogen. Tetrahydrofuran (25 mL) and a weighed amount of an internal standard were added by syringe. This vessel was placed in an ice bath, and, with efficient stirring, a solution of *sec*-butyllithium or *n*-butyllithium (6.00 mmol) was injected by syringe. The resulting mixture was stirred for 30 min at 0 °C before it was cooled to −78 °C and 0.284 g (1.00 mmol) of *n*-octyl tosylate was injected. After 1 h of stirring at −78 °C, this mixture was allowed to warm to room temperature whereupon it was stirred for an additional 2 h before being subjected to the workup described above.

R = *tert*-Butyl (Typical Procedure). The above procedure was modified slightly to accommodate the decreased thermal stability of the organocopper(I) reagent. Thus, *tert*-butyllithium (3.85 mL, 6.00 mmol) was added to a suspension of copper iodide in (3.00 mmol) in THF at 0 °C with stirring. The resulting mixture was stirred for 15 min and then cooled to −78 °C and treated with 1-bromooctane (0.193 g, 1.00 mmol).

2,2-Dimethyldecane (Preparative-Scale Procedure). Into a flame-dried, three-necked 500-mL flask equipped with a Teflon-coated stirring bar and a 50-mL addition funnel and capped with rubber septums was placed copper(I) iodide (6.66 g, 35.0 mmol) and THF (250 mL). This mixture was cooled to −5 °C and a solution of *tert*-butyllithium (41.3 mL, 60.0 mmol) was added dropwise over a period of 5 min. The dark solution was stirred between 0 °C and −5 °C for 15 min and then cooled to −78 °C and 1-bromooctane (1.88 g, 9.77 mmol) was added dropwise by syringe. This mixture was stirred at −78 °C for 2 h and then at room temperature for an additional 12 h. The resulting mixture was treated with 80 mL of 3 N HCl and filtered through a Kieselguhr mat, and the layers were separated. The organic phase was washed with two 50-mL portions of 3 N HCl and then with two 50-mL portions of saturated brine. The aqueous phase and washings were extracted with two 50-mL portions of petroleum ether, and the combined organic phases were dried ($MgSO_4$), concentrated, and distilled (bulb-to-bulb, 2.3 torr) yielding 1.60 g of a colorless liquid which GLPC analysis indicated to be ~80% 2,2-dimethyldecane.

Oxidation Procedures. Similar procedures were employed in all oxidation reactions. The following examples are typical.

The reaction mixture produced by the addition of a solution of *sec*-butyllithium (4.92 mL, 6.00 mmol) to a suspension of copper(I) iodide (6.57 g, 3.00 mmol) in THF prepared as described above was cooled to −78 °C. A stream of dry dioxygen was bubbled rapidly, with efficient stirring, through the solution for 5 min. The resulting mixture was allowed to warm to room temperature and treated as previously described prior to analysis of GLPC.

Oxidation with nitrobenzene (1.85 g) at −78 °C gave a mixture which was mixed thoroughly, then allowed to warm to ambient temperature, and treated as previously described prior to analysis by GLPC.

Reaction of 8 (R = *sec*-C_4H_9) with Methyl Ethyl Ketone. The reagent 8 (3.00 mmol, R = *sec*-butyl) prepared at 0 °C in THF (25 mL) and a weighed amount of internal standard were cooled to −78 °C and methyl ethyl ketone (63.0 mg, 0.886 mmol) was added by syringe. The resulting mixture was stirred at −78 °C for 1 h and then at ambient temperature for an additional 1.5 h. An aliquot of the mixture was removed and treated with 0.2 mL of water; the resulting solids were compacted by centrifugation and the supernatant solution was analyzed by GLPC.

Acknowledgments. This work was supported by the National Science Foundation (Grant 77-08331).

Registry No. 8 (R = *tert*-C_4H_9), 23402-75-7; 8 (R = *sec*-C_4H_9), 23402-73-5; 8 (R = C_4H_9), 24406-16-4; $C_8H_{17}Cl$, 111-85-3; $C_8H_{17}Br$, 111-83-1; $C_8H_{17}I$, 629-27-6; 2-chlorooctane, 628-61-5; 2-bromooctane, 557-35-7; 2-iodooctane, 557-36-8; 2-octyl tosylate, 1028-12-2; octyl tosylate, 3386-35-4; nonane, 111-84-2; 2-methyloctane, 3221-61-2; dodecane, 112-40-3; 5-methylundecane, 1632-70-8; 3-methylundecane, 1002-43-3; 2,2-dimethyldecane, 17302-37-3; 1-phenyloctane, 2189-60-8; 2-cyclohexen-1-one, 930-68-7; methyl vinyl ketone, 78-94-4; 3-methylcyclohexanone, 591-24-2; 3-butyl-2-cyclohexenone, 6301-49-1; 3-*tert*-butylcyclohexanone, 936-99-2; 2-octanone, 111-13-7; 2,2,3-trimethylnonane, 55499-04-2; 3,4-dimethyldecane, 17312-45-7; CuI, 7681-65-4; tetrakis[iodo(tributylphosphine)copper(I)], 28132-72-1; 5-methyl-5-undecanol, 21078-80-8; 3-*tert*-butylphenol, 585-34-2; 3-*tert*-butylcyclohexanol, 4534-70-7; iodo[bis(dibutyl sulfide)copper(I)], 35907-81-4; methyl ethyl ketone, 78-93-3; 3,4-dimethyl-3-hexanol, 19550-08-4; octane, 111-65-9; 3,4-dimethylhexane, 583-48-2.

1-Aryl-8-tropylionaphthalene Perchlorates: Synthesis and Intramolecular Charge-Transfer Interaction

Koichi Komatsu, Nobuyuki Abe, Kenji Takahashi, and Kunio Okamoto*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received February 22, 1979

A series of 1-aryl-8-tropylionaphthalene cations [aryl = phenyl (**4a**), *p*-methylphenyl (**4b**), *m,m*-dimethylphenyl (**4c**), *p*-methoxyphenyl (**4d**), *p*-(trifluoromethyl)phenyl (**4e**), and *m,m*-bis(trifluoromethyl)phenyl (**4f**)] have been synthesized by nickel(II)-catalyzed coupling of 1-bromo-8-cycloheptatrienylnaphthalene with the corresponding arylmagnesium halides followed by hydride abstraction. The ^1H NMR spectra of **4a–f** indicated that the two aromatic rings at the peri positions are in a face-to-face arrangement. The absorption band at 373 nm observed in the electronic spectrum of **4a** in acetonitrile was assigned to the intramolecular charge-transfer band between the phenyl and tropylium rings based on the solvent and substituent effects. This intramolecular electronic interaction results in stabilization of the cation **4a** by 2.1 pK_{R^+} units and the increase in its reduction potential by 0.182 V as compared with the reference cation, 1-tropylionaphthalene (**5**). A better linear correlation was obtained when the values of pK_{R^+} and reduction potential for **4a–f** were plotted against the substituent constant σ_m^+ rather than against σ_p^+. This result together with the substituent effect upon the ^1H NMR chemical shift of the tropylium ring protons suggests that the electronic effect of the substituents would be transmitted inductively through the σ overlap of p orbitals of the two aromatic rings facing each other.

There has been considerable interest in the *intra*molecular charge-transfer complex,[1-3] since it can be regarded as an undissociable donor–acceptor pair, and thus serves as the most fundamental model system for the study of *inter*molecular charge-transfer interaction. Recently, a strong π acceptor with a full positive charge, the tropylium ion, was shown to be an effective probe to detect the

---

(1) For example, see (a) D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1227 (1966); (b) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971); (c) W. Rebafka and H. A. Staab, *Angew. Chem.*, **85**, 831 (1973); **86**, 234 (1974); (d) H. A. Staab and U. Zapf, *ibid.*, **90**, 807 (1978), and the earlier publications cited therein; (e) H. Tatemitsu, B. Natsume, M. Yoshida, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3459 (1978), and the earlier publications cited therein; (f) R. Luhowy and P. M. Keehn, *J. Am. Chem. Soc.*, **99**, 3797 (1977), and the references cited therein; (g) Y. Fukazawa, M. Aoyagi, and S. Ito, *Tetrahedron Lett.*, 1067 (1978); (h) T. Nakazawa, Y. Niimoto, and I. Murata, *ibid.*, 569 (1978).

(2) (a) J. G. O'Connor and P. M. Keehn, *J. Am. Chem. Soc.*, **98**, 8446 (1976); (b) H. Horita, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3899 (1976); (c) H. Horita, T. Otsubo, and S. Misumi, *Chem. Lett.*, 807 (1978).

(3) (a) T. Nakazawa and I. Murata, *J. Am. Chem. Soc.*, **99**, 1996 (1977); (b) D. N. Butler and I. Gupta, *Can. J. Chem.*, **56**, 80 (1978).

0022-3263/79/1944-2712$01.00/0