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Direct Formation of (Haloaryl)copper Nucleophiles from Haloiodobenzenes and Active Copper

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(*o*-Halophenyl)-, (*m*-halophenyl)-, and (*p*-halophenyl)copper reagents have been formed in moderate to high yields at room temperature from active copper and the corresponding haloiodobenzenes. These reagents have been cross-coupled with a variety of alkyl and acyl halides to produce the respective haloarenes and haloaryl ketones. Remarkably, (*o*-fluorophenyl)- and (*o*-chlorophenyl)-copper are produced in good yields by this procedure without undergoing elimination to form benzyne making this approach a convenient method for generating *o*-halophenyl nucleophiles.

Introduction

The haloaryl species is an important synthetic fragment often incorporated into biologically active compounds and potential medicinal drugs.[1] The synthetic route commonly employed is Friedel−Crafts alkylation or acylation which frequently lacks regiospecificity.[2] In contrast, there is usually a high degree of regiospecificity in the reactions of haloaryl nucleophiles with suitable substrates. (Haloaryl)copper reagents are obvious nucleophiles of choice since they undergo substitution[3] with great facility and have a high tolerance for many functional groups.[4]

Many other haloaryl organometallics are known but they frequently prove difficult to prepare, persist only at low temperatures, or do not cross-couple with the facility shown by organocopper compounds.[5] With care, (*m*-haloaryl)- and (*p*-haloaryl)lithium and Grignard reagents can be prepared from the corresponding haloiodobenzenes[5b] or dihalobenzenes[5c] which, in turn, can be converted into other organometallics by treatment with salts of less reactive metals.[6]

o-Haloaryl nucleophiles have traditionally been produced at low temperature by oxidative addition of lithium or magnesium to 1,2-dihalobenzenes or by treatment of halobenzenes with strong base.[7,8] Only at low temperatures, often approaching −100 °C, do these reagents persist in significant quantity.[7,8] At higher temperatures the resulting intermediates typically undergo a very facile 1,2-elimination to form benzyne.[5b,9] Recently, in spite of these difficulties, Lipshutz and co-workers[10] and Widdowson et al.[11] have successfully utilized (*o*-halophenyl)copper reagents prepared by low-temperature transmetalation of the corresponding (*o*-halophenyl)lithium compounds.

Active Copper

Rieke[12] and Ebert[13] have developed a highly activated copper which permits the direct formation of a wide variety of organocopper compounds from the respective organic halides without utilizing traditional organolithium or Grignard precursors.[5,14,15] This active copper is prepared by reducing under argon an ethereal solution of $\mathrm{CuI{\cdot}PR_3}$ with an ethereal solution of preformed lithium naphthalenide or biphenylide. The resulting copper is sufficiently reactive to allow direct oxidative addition to alkyl and aryl halides (eqs 1 and 2).

$$\mathrm{Li^+\ nap^{\bullet-} + CuI{\cdot}PR_3 \rightarrow Cu^0 + nap + PR_3 + LiI} \tag{1}$$

$$\mathrm{2Cu^0 + RX \rightarrow CuR + CuX} \tag{2}$$

In recent work, Rieke and co-workers have examined the reduction of other copper salts to produce an active

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⊛ Abstract published in *Advance ACS Abstracts*, March 1, 1995.

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[2] For an introduction to this topic see: March, J. *Advanced Organic Chemistry Reactions, Mechanisms, and Structure*, 4th ed.; Wiley: New York, 1992; pp 534−542.

[3] For leading papers and reviews see: (a) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245. (b) Corey, E. J.; Katzenellenbogen, J. A.; Roman, S. A.; Gilman, H. W. *Tetrahedron Lett.* **1971**, 1821. (c) Posner, G. H. *Org. React.* **1975**, *22*, 253. (d) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (e) Lipshutz, B. H.; *Synthesis* **1987**, 325.

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[6] For an introduction to this topic see: Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: New York, 1988; p 20.

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Table 1. Formation of (3-Haloaryl)- and (4-Haloaryl)copper Reagents 2 from the Respective Haloiodobenzenes 1 and Activated Copper[a]

$$\underset{\mathbf{1}}{XC_6H_4I} \xrightarrow{Cu^0} \underset{\mathbf{2}}{[XC_6H_4Cu]} \xrightarrow{H^+} \underset{\mathbf{3}}{XC_6H_5}$$

no.	orientation	X	Cu^0/RX^b	time (min)	% yield[c] of **3**
1a	*para*	F	2.5/1	10	81
1b	*para*	Cl	2/1	10	69
1c	*para*	Br	2/1	30	60
1d	*meta*	F	2.5/1	10	85
1e	*meta*	Cl	2/1	10	78
1f	*meta*	Br	2/1	60	78

[a] All reactions were run under argon in THF or DME at 25 °C. The active copper was derived from the reduction of $CuI{\cdot}P(Et)_3$. [b] Denotes the Cu^0/XC_6H_4I ratio. [c] Quantitation was by GC. The yield of **3** found after quenching the reaction was assumed to be indicative of the amount of organocopper **2** present at the time of the quench.

copper. These include the low-temperature reduction of $CuCN{\cdot}2LiBr$,[16] the reduction of lithium 2-thienylcyanocuprate,[17] and the 2 equiv reduction of Cu(I) complexes to form copper anion complexes.[18] Each of these methods produces an active form of copper although the degree of reactivity and general synthetic utility for each of these approaches varies considerably.

In our own laboratory we have focused on developing functionalized organocopper compounds by the use of active copper derived from the reduction of $CuI{\cdot}PR_3$ and have examined the formation of ketone-[13b] and ester-functionalized[13c] organocopper reagents. Recently, we communicated a preliminary and rather remarkable finding that (*o*-fluorophenyl)- and (*o*-chlorophenyl)copper reagents could be produced in good yields at room temperature by the direct oxidative addition of active copper to the respective *o*-haloiodobenzenes without undergoing any significant elimination.[19] We have now completed our initial study of the formation of (haloaryl)-copper reagents in general and herein report the findings.

Results and Discussion

3-Halo- and 4-Haloiodobenzenes. These compounds undergo a facile oxidative addition with activated copper to produce the corresponding (haloaryl)copper reagents in good yields (Table 1). Since the halogen is not adjacent to copper, a subsequent β-elimination of CuX is not a concern. As a result the precise reaction time and temperature are not unduly critical.

In turn, these reagents undergo cross-coupling with a wide variety of alkyl and acyl halides to produce the corresponding haloarenes and haloaryl ketones (Table 2). Most yields are moderate to good. Interestingly, the results vary more widely for the (4-haloaryl)copper reactions than for the 3-haloaryl counterparts. This may be due to the stronger mesomeric effect exerted on the nucleophilic carbon by halogens in the *para* position relative to *meta*.

Table 2. Cross-Coupling Reactions of (3-Haloaryl)- and (4-Haloaryl)copper Reagents[a]

$$\underset{\mathbf{2}}{XC_6H_4Cu} + RX' \rightarrow XC_6H_4R$$

4: X = 3-halo
5: X = 4-halo

XC_6H_4Cu	solvent	RX′	no.	product	% yield[b] of **4, 5**
m-F	THF	CH_3I	**4a**	*m*-$FC_6H_4CH_3$	49 (42)
m-F	THF	$PhCH_2Br$	**4b**	*m*-$FC_6H_4CH_2Ph$	54 (46)
m-F	THF	EtI	**4c**	*m*-FC_6H_4Et	31 (26)
m-F	DME	$CH_3(CO)Cl$	**4d**	*m*-$FC_6H_4(CO)CH_3$	59 (50)
m-Cl	THF	CH_3I	**4e**	*m*-$ClC_6H_4CH_3$	61 (48)
m-Cl	THF	EtI	**4f**	*m*-ClC_6H_4Et	93 (72)
m-Cl	THF	$PhCH_2Br$	**4g**	*m*-$ClC_6H_4CH_2Ph$	90 (70)
m-Cl	DME	$CH_3(CO)Cl$	**4h**	*m*-$ClC_6H_4(CO)CH_3$	94 (74)
m-Cl	DME	PhCOCl	**4i**	*m*-$ClC_6H_4(CO)Ph$	92 (72)
m-Br	THF	CH_3I	**4j**	*m*-$BrC_6H_4CH_3$	58 (45)
m-Br	THF	EtI	**4k**	*m*-BrC_6H_4Et	45 (35)
m-Br	DME	$CH_3(CO)Cl$	**4l**	*m*-$BrC_6H_4(CO)CH_3$	91 (71)
m-Br	DME	Ph(CO)Cl	**4m**	*m*-$BrC_6H_4(CO)Ph$	82 (64)
p-F	THF	CH_3I	**5a**	*p*-$FC_6H_4CH_3$	56 (45)
p-F	THF	EtI	**5b**	*p*-FC_6H_4Et	63 (51)
p-F	THF	$PhCH_2Br$	**5c**	*p*-$FC_6H_4CH_2Ph$	77 (62)
p-F	DME	Ph(CO)Cl	**5d**	*p*-$FC_6H_4(CO)Ph$	76 (61)
p-F	DME	$CH_3(CO)Cl$	**5e**	*p*-$FC_6H_4(CO)CH_3$	12 (10)
p-Cl	THF	CH_3I	**5f**	*p*-$ClC_6H_4CH_3$	60 (42)
p-Cl	THF	EtI	**5g**	*p*-ClC_6H_4Et	71 (49)
p-Cl	THF	$CH_3(CH_2)_3I$	**5h**	*p*-$ClC_6H_4(CH_2)_3CH_3$	56 (38)
p-Cl	DME	Ph(CO)Cl	**5i**	*p*-$ClC_6H_4(CO)Ph$	80 (55)
p-Cl	DME	$CH_3(CO)Cl$	**5j**	*p*-$ClC_6H_4(CO)CH_3$	19 (13)
p-Br	THF	CH_3I	**5k**	*p*-$BrC_6H_4CH_3$	55 (34)
p-Br	THF	EtI	**5l**	*p*-BrC_6H_4Et	65 (39)
p-Br	THF	$CH_3(CH_2)_3I$	**5m**	*p*-$BrC_6H_4(CH_2)_3CH_3$	50 (30)
p-Br	DME	Ph(CO)Cl	**5n**	*p*-$BrC_6H_4(CO)Ph$	57 (34)
p-Br	DME	$CH_3(CO)Cl$	**5o**	*p*-$BrC_6H_4(CO)CH_3$	46 (28)

[a] All substitutions were run under argon for 30 min at 25 °C with a 3-fold excess of RX′. [b] Quantitation was by GC. The first value represents the yield based upon the amount of organocopper **2** present just prior to the addition of RX′. The second value (in parentheses) represents the overall yield from starting material.

Table 3. Formation of (2-Halophenyl)copper Reagents 7 from (2-Haloiodobenzenes 6 and Activated Copper[a]

$$\underset{\mathbf{6}}{o\text{-}XC_6H_4I} \xrightarrow{Cu^0} \underset{\mathbf{7}}{[o\text{-}XC_6H_4Cu]} \xrightarrow{H^+} \underset{\mathbf{3}}{XC_6H_5}$$

compd	X	temp, °C	% yield[b] of **3**
6a	F	25	76
6b	Cl	25	74
6C	Br	−78	34[c]

[a] All reactions were run under argon in THF or DME. The $Cu^0/o\text{-}XC_6H_4I$ ratio was 2/1, and the active copper was derived from the reduction of $CuI{\cdot}P(Et)_3$. Reactions were found to be complete within 10 min. [b] Quantitation was by GC. The yield of **3** found after quenching the reaction was assumed to be indicative of the amount of organocopper **7** present at the time of the quench. [c] Yields varied from 5% to 34%.

2-Haloiodobenzenes. Upon examining the reaction with 2-haloiodobenzenes we were pleased to find that, with the exception of 2-bromoiodobenzene, the respective (2-halophenyl)copper reagents could be easily produced in good yields at room temperature (Table 3). In comparison, yields for (2-bromophenyl)copper (**6c**) were low and difficult to reproduce ranging from a high of 34%

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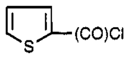
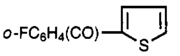
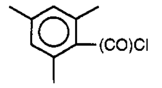
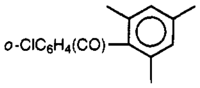
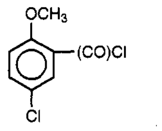
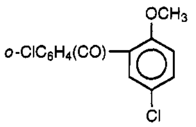
Table 4. Cross-Coupling Reactions of (2-Halophenyl)copper Reagents[a]

$$\underset{\mathbf{7}}{o\text{-}XC_6H_4Cu} + RX' \rightarrow \underset{\mathbf{8}}{o\text{-}XC_6H_4R}$$

X	solvent	RX′	no.	product **8**	% yield[b] of **8**
F	THF	CH_3I	**8a**	*o*-$FC_6H_4CH_3$	100 (76)
F	THF	EtI	**8b**	*o*-FC_6H_4Et	98 (74)
F	THF	$PhCH_2Br$	**8c**	*o*-$FC_6H_4CH_2Ph$	90 (65)
F	DME	Ph(CO)Cl	**8d**	*o*-$FC_6H_4(CO)Ph$	96 (73)
F	DME	$CH_3(CO)Cl$	**8e**	*o*-$FC_6H_4(CO)CH_3$	75 (57)
Cl	THF	CH_3I	**8f**	*o*-$ClC_6H_4CH_3$	77 (57)
Cl	THE	CH_3CH_2I	**8g**	*o*-$ClC_6H_4CH_2CH_3$	93 (69)
Cl	THF	$PhCH_2Br$	**8h**	*o*-$ClC_6H_4CH_2Ph$	96 (61)
Cl	THF	Ph(CO)Cl	**8i**	*o*-$ClC_6H_4(CO)Ph$	81 (60)
Cl	DME	$CH_3(CO)Cl$	**8j**	*o*-$ClC_6H_4(CO)CH_3$	88 (65)
Br	THE	CH_3I	**8k**	*o*-$BrC_6H_4CH_3$	26 (9)
Br	DME	Ph(CO)Cl	**8l**	*o*-$BrC_6H_4(CO)Ph$	31 (10)
F	DME		**8m**		87 (53)
Cl	DME		**8n**		88 (56)
Cl	DME		**8o**		94 (70)

[a] All reactions were run under argon for 30 min with a 3-fold excess of RX′. Reactions with *o*-F and *o*-Cl were performed at 25 °C. Reactions with *o*-Br were carried out at −78 °C for 30 min and then allowed to slowly warm to room temperature. [b] Quantitation was by GC. The first value represents the yield based upon the amount of organocopper (**7**) present just prior to the addition of RX′. The second value (in parentheses) represents the overall yield from starting material.

when the reaction was conducted at −78 °C to a low of 5% when the reaction was carried out at 25 °C.

It seems probable that (*o*-bromophenyl)copper is initially formed and then undergoes elimination to produce benzyne and copper(I) bromide. The analogous elimination by (2-bromophenyl)lithium or -magnesium is thoroughly documented.[7b] The stronger carbon−halogen bond in (2-chlorophenyl)- and (2-fluorophenyl)copper apparently increases the activation energy to the extent that elimination is curtailed at 25 °C for these compounds.

The (2-halophenyl)copper intermediates participate in substitution reactions with suitable alkyl halides and acyl chlorides to form the corresponding 2-haloarenes and 2-haloaryl ketones (Table 4). The yields are high except for reactions with (2-bromophenyl)copper (**8k**,**l**). Several attempts failed to couple more than 31% of the brominated organocopper intermediate.

Applications. The ability to easily produce (haloaryl)copper nucleophiles in good yields opens the door to new synthetic routes for a variety of interesting and important compounds having commercial and biochemical applications as shown at the bottom of Table 4. (2-Fluorophenyl)copper will cross-couple with 2-thiophenecarbonyl chloride to produce 2,2′-fluorobenzoylthiophene (**8m**) in 87% yield. This product has been used as a replacement for tienilic acid in the development of an assay for 5-hydroxylation reactions by rat liver microsomes.[20] (2-Chlorophenyl)copper reacts with 2,4,6-trimethylbenzoyl chloride to form 2′-chloro-2,4,6-trimethylbenzophenone (**8n**) in 88% yield. This compound is part of a mixture found in thermal recording materials and is utilized in thermal printing.[21] As a final example, (2-chlorophenyl)copper was cross-coupled with 4-chloro-2-methoxybenzoyl chloride to produce 2′,4-dichloro-2-methoxybenzophenone (**8o**) in 95% yield. This product (and similar analogs) undergoes cyclization with metal sulfides to produce xanthones which can function as photoinitiators for select polymerizations.[22]

Conclusions

In conclusion, a practical new method for generating haloarylcopper nucleophiles at room temperature has been established. (*m*-haloaryl)- and (*p*-haloaryl)copper reagents and, most notably, (*o*-fluorophenyl- and (*o*-chlorophenyl)copper reagents can be synthesized in good yields directly from active copper and the respective haloiodobenzenes at 25 °C without serious loss due to competing elimination. The organocopper compounds can be utilized in subsequent substitution reactions to produce haloaryl cross-coupled products. This approach does not suffer from the lack of regiospecificity commonly found for Friedel−Crafts reactions making the activated copper approach one of the methods of choice for the synthesis of many haloarenes and haloaryl ketones.

Experimental Section

General. Our basic laboratory procedures, experimental setup, method of gas chromatography analysis, formation of lithium naphthalenide and biphenylide, formation of $CuI\cdot P(Et)_3$, formation of activated copper, and workup and identification procedures have all been previously reported in detail.[13a]

Starting Materials. All chemicals purchased were reagent grade or better and used as received.

Typical Experimental Procedure. All reactions were carried out in 50-mL two-neck round-bottomed flasks equipped with a reflux condenser and rubber septum and containing a small Teflon-clad stirring bar. The condenser was connected to an argon vacuum manifold via a tubing connector. The oven-dried glassware was placed in a glovebox and charged with Li (11 mmol, small chips from lithium rod, Aldrich) and either naphthalene or biphenyl (12 mmol) and then attached to the argon vacuum manifold. Freshly distilled THF or DME (15−25 mL) was syringed into the flask, and stirring commenced. When the reduction was complete (2−3 h) a mixture of $CuI\cdot P(Et)_3$[23] (10 mmol) in THF or DME (5−10 mL) was injected into the lithium naphthalenide or biphenylide solution. After 5 min the formation of the brownish red suspension of activated copper was complete. The temperature of the suspension was adjusted as necessary (see Tables 1−4 for specific values) after which the haloaryl iodide was added (5 mmol) along with an internal standard (typically decane, 2 mmol). The solution was stirred until the maximum yield of organocopper intermediate was obtained (10−60 min, see Tables 1−4). An aliquot (0.5 mL) of the solution was removed and analyzed to obtain the yield of organocopper intermediate. The cross-coupling substrate (15 mmol) was then added and the solution stirred for an additional 30 min. The yield of cross-coupled product was determined by GC analysis using the internal standard method. Authentic samples of the products were used to obtain accurate response factors. Most of the starting ha-

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loiodobenzene which was not converted to product was present as unreacted starting material.

Workup and Analysis. The contents of the reaction flask (typically 20–45 mL) were poured into HCl (0.1 M, 50 mL). Methylene chloride was added (25 mL), and the layers were separated. The organic layer was washed twice with HCl (0.1 M, 25 mL), once with water, and dried over $MgSO_4$. Volatile components were isolated by either fractional distillation or preparative GC. Higher boiling components were isolated by flash chromatography after being separated from the more volatile compounds by rotary evaporation. Products were identified by their physical and spectral properties. Triethylphosphine contaminants were removed for the most part by the acid washings. The small residual contamination, when present, was completely removed from the products by the subsequent distillation or use of flash chromatography. Compounds synthesized in this work have been previously reported in the literature[24] and most are commercially available.

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Supplementary Material Available: Spectroscopic and analytical data for all products (7 pages). This material is contained in libraries on microfiche, immediately following the article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) One apparent exception is 1-chloro-3-ethylbenzene, which does not appear to have been previously reported.