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Carboxylation and Esterification of Functionalized Arylcopper Reagents[§]

Greg W. Ebert,* Wayne L. Juda, Robert H. Kosakowski, Bing Ma, Liming Dong,
Keith E. Cummings, Mwita V. B. Phelps, Adel E. Mostafa, and Jianyuan Luo

*Department of Chemistry, State University of New York College at Buffalo, 1300 Elmwood Avenue,
Buffalo, New York 14222*

ebertgw@bscmail.buffalostate.edu

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$$\text{G-ArI} \xrightarrow{\text{Cu}^*} \text{G-ArCu} \xrightarrow{\text{CO}_2} \text{G-ArCOOCu} \xrightarrow{\text{RX}} \text{G-ArCOOR}$$

G = ester, ketone, nitrile, halogen

Functionalized arylcopper reagents have been produced in good yields at 25 °C from activated copper and the corresponding functionalized aryl iodides without the need of traditional organolithium or Grignard precursors. These organocopper compounds will undergo carboxylation with CO_2 to form the corresponding copper benzoates. In turn, these salts can be acidified to produce the functionalized aryl acids or treated with appropriate alkyl halides in the presence of a dipolar aprotic solvent to generate the corresponding aryl esters. This methodology permits the formation of functionalized organic acids and esters that could not be generated by the carboxylation of organomagnesium compounds.

Introduction

The importance of functionalized benzoic acid and ester derivatives in the realm of organic chemistry cannot be overemphasized. From natural products to pharmaceuticals and from protective coatings to synthetic fibers, these compounds play a major role.[1]

The carboxylation of arylcopper reagents is a useful approach to the synthesis of aryl acids and derivatives. The position of the entering carboxyl group during carbonation is unambiguous, the reaction conditions are quite mild, yields are usually excellent with few side reactions, and the resulting copper carboxylates can be subsequently converted into esters and other acid derivatives within the same reaction vessel.[2] If, however, the arylcopper reagents were produced by the active copper approach, a wide variety of functionality could be incorporated into the arylcopper reagents, which would not be possible if traditional lithium and Grignard precursors were employed. The ability to carboxylate and subsequently esterify *functionalized* arylcopper reagents would raise the status of this carbonation reaction from "merely useful" to "extremely attractive" as illustrated:

$$\text{G-ArI} \xrightarrow{\text{Cu}^0} \text{G-ArCu} \xrightarrow{\text{CO}_2} \text{G-ArCOOCu} \xrightarrow{\text{RX}} \text{G-ArCOOR} \tag{1}$$

where G = ester, ketone, nitrile, halogen, etc. It would permit the formation of a variety of functionalized benzoic acids and derivatives, some of which would be very difficult to synthesize by other methods. This approach would compliment many of the other existing methods for producing aryl acids and derivatives and in many cases would have definite advantages in terms of the scope and the conditions of reaction.

While several methods exist for carboxylating organic compounds, many of the approaches are of limited scope and applicability. Organocadmium,[3] zinc,[3] and aluminum[4] compounds are resistant to carboxylation unless the reactions are run at elevated temperatures and pressures. The Kolbe−Schmitt synthesis[5] and the Henkel reaction[6] both require high temperature and pressure. The oxidation of arenes also requires harsh conditions employing strong oxidants such as $KMnO_4$ or $K_2Cr_2O_7$

[§] Dedicated to Professor Reuben D. Rieke in honor of his academic retirement and for his career in pioneering work on the activation of metals for organic synthesis.

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at elevated temperatures.[7] In contrast, the carboxylation of arylcuprates takes place at room temperature and 1 atm.

Several workers have developed reactions of transition-metal carbonyl catalysts capable of producing acids and esters from suitable feedstocks. The $Na_2Fe(CO)_4$ system was studied by Cooke and Collman,[8] $NaCo(CO)_4$ by Heck et al.,[9] and $Ni(CO)_4$ by Tsutsumi and co-workers[10] to name a few. In most cases aliphatic acids and esters could be produced in high yields, but vinyl and aryl systems were unreactive.[8,9] The nickel catalyst is capable of producing aryl acids but suffers from the drawback of the acute toxicity of $Ni(CO)_4$.[10] By comparison, arylcopper compounds readily undergo carboxylation with CO_2 and the toxicity of copper salts is much less than that of nickel compounds.

Aryllithium and Grignard reagents tend to react with their carbonated analogues to produce side products consisting of ketones and tertiary alcohols unless a large excess of CO_2 is employed and care is taken.[11] In addition, the high reactivity of these organometallics severely limits the functionality that can be incorporated into these reagents. It is for this reason that arylcopper compounds produced from these traditional precursors offer little advantage over the lithium and Grignard compounds themselves. However, the synthesis of arylcopper reagents via the active copper approach does not suffer from these constraints and such reagents can tolerate a wide variety of functionality.

Active Copper. Rieke[12] and Ebert[13] have developed a highly active copper, which allows the direct formation of a wide variety of organocopper reagents from the respective organic halides without utilizing traditional organolithium or Grignard precursors.[14−16] This activated copper is formed by reducing under argon an ethereal solution of $CuI{\cdot}PR_3$ 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:

$$Li^+\ nap^- + CuI{\cdot}PR_3 \rightarrow Cu^0 + nap + PR_3 + LiI \quad (2)$$

$$2Cu^0 + RX \rightarrow CuR + CuX \quad (3)$$

In more recent work, Rieke and co-workers have studied the reduction of other copper salts to produce an activated copper. These include the reduction of lithium 2-thienylcyanocuprate,[17] the 2 equiv reduction of Cu(I) complexes to form copper anion complexes,[18] and the low-temperature reduction of $CuCN{\cdot}_2LiBr$.[19] Each of these methods will produce an activated 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 produced from the reduction of $CuI{\cdot}PR_3$ and have most recently completed a study on the formation and reaction of (haloaryl)copper nucleophiles produced from haloiodobenzenes and active copper.[20] In the work presented here we study the carboxylation and subsequent esterification of functionalized arylcopper compounds and examine the advantages such a scheme offers.

Results and Discussion

The carboxylation of functionalized arylcopper compounds is accomplished in moderate to good yields as illustrated in Table 1. The reaction conditions are mild and a wide variety of functionality can be tolerated in the arylcopper reagent without adverse effects. When direct comparisons are made, the product yields for the various isomeric benzenes follow the general order ortho > para > meta. This is expected on the basis of the well-known "ortho effect" that has been noted for both the formation and reactions of arylcopper compounds.[21] The reason for the low yield conversion of 4-cupriobenzophenone to the corresponding acid is not readily apparent, and efforts to increase this yield are ongoing.

A wide variety of alkyl halides can be used to esterify cuprio 2-fluorobenzoate in moderate to good yields as shown in Table 2. The precise mechanism for this reaction has not yet been determined and may vary depending upon the alkyl halide.[2b,c,22−23] Although a

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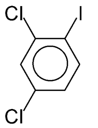
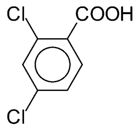
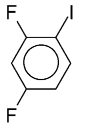
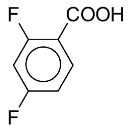
TABLE 1. Carboxylation of Functionalized Arylcopper Compounds

$$\underset{\mathbf{1}}{\text{G-ArI}} \xrightarrow{\text{Cu}^{\text{O}}} \underset{\mathbf{2}}{\text{G-ArCu}} \xrightarrow{\text{CO}_2} \underset{\mathbf{3}}{\text{G-ArCOOCu}} \xrightarrow{\text{H}^+} \underset{\mathbf{4}}{\text{G-ArCOOH}}$$

no.	Reactant **1**	no.	product **4**	% yield^a of **4**
1a	o-FC_6H_4I	**4a**	o-FC_6H_4COOH	99 (78)
1b	m-FC_6H_4I	**4b**	m-FC_6H_4COOH	50 (31)
1c	p-FC_6H_4I	**4c**	p-FC_6H_4COOH	69 (42)
1d	o-ClC_6H_4I	**4d**	o-ClC_6H_4COOH	85 (75)
1e	m-ClC_6H_4I	**4e**	m-ClC_6H_4COOH	25 (15)
1f	p-ClC_6H_4I	**4f**	p-ClC_6H_4COOH	74 (55)
1g	m-BrC_6H_4I	**4g**	m-BrC_6H_4COOH	99 (49)
1h	p-BrC_6H_4I	**4h**	p-BrC_6H_4COOH	87 (44)
1i	o-$CH_3OOCC_6H_4I$	**4i**	o-$CH_3OOCC_6H_4COOH$	95 (79)
1j	m-$CH_3OOCC_6H_4I$	**4j**	m-$CH_3OOCC_6H_4COOH$	73 (35)
1k	p-$CH_3OOCC_6H_4I$	**4k**	p-$CH_3OOCC_6H_4COOH$	85 (61)
1l	o-NCC_6H_4Br	**4l**	o-NCC_6H_4COOH	87 (57)
1m	p-NCC_6H_4Br	**4m**	p-NCC_6H_4COOH	60 (40)
1n	p-$C_6H_5C(O)C_6H_4I$	**4n**	p-$C_6H_5C(O)C_6H_4CO_2H$	15 (7)
1o		**4o**		94 (74)
1P		**4P**		95 (76)

[a] The first value represents the yield based upon the amount of organocopper (**2**) present just prior to the addition of CO_2. The second value (in parentheses) represents the overall yield from starting material (**1**).

TABLE 2. Esterification of Copper *o*-Fluorobenzoate

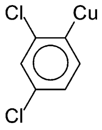
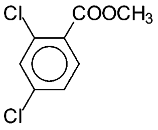
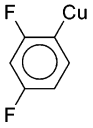
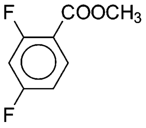
$$\underset{\mathbf{3a}}{o\text{-F-ArCOOCu}} + \underset{\mathbf{5}}{\text{RX}} \xrightarrow[\text{THF/(DMF or DMSO)}]{65^{\circ}\text{C, 4hrs.}} \underset{\mathbf{6}}{o\text{-F-ArCOOR}}$$

no.	RX	no.	% Yield^a of **6**
5a	CH_3I	**6a**	92 (87)
5b	CH_3CH_2I	**6b**	99 (87)
5c	$PhCH_2Br$	**6c**	59 (43)
5d	$CH_2{=}CHCH_2Br$	**6d**	95 (75)
5e	CH_3CHICH_3	**6e**	76 (57)
5f	$(CH_3)_3CI$	**6f**	57 (45)

[a] Quantitative results were obtained by GC analyses. The first value represents the yield based upon the amount of organocopper (**2a**) present just prior to the addition of CO_2. The second value (in parentheses) represents the overall yield from starting material (**1a**).

TABLE 3. Methyl Esterification of Functionalized Copper Benzoates

$$\underset{\mathbf{1}}{\text{G-ArI}} \xrightarrow{\text{Cu}^{\text{O}}} \underset{\mathbf{2}}{\text{G-ArCu}} \xrightarrow{\text{CO}_2} \underset{\mathbf{3}}{\text{G-ArCOOCu}} \xrightarrow{\text{CH}_3\text{I}} \underset{\mathbf{7}}{\text{G-ArCOOCH}_3}$$

no.	organocopper **2**	no.	ester **7**	% Yield^a of **7**
2d	o-ClC_6H_4Cu	**7d**	o-$ClC_6H_4COOCH_3$	59 (44)
2i	o-$CH_3OOCC_6H_4Cu$	**7i**	o-$CH_3OOCC_6H_4COOCH_3$	90 (70)
2j	m-$CH_3OOCC_6H_4Cu$	**7j**	m-$CH_3OOCC_6H_4COOCH_3$	63 (32)
2k	p-$CH_3OOCC_6H_4Cu$	**7k**	p-$CH_3OOCC_6H_4COOCH_3$	80 (60)
2l	o-NCC_6H_4Cu	**7l**	o-$NCC_6H_4COOCH_3$	95 (54)
2m	p-NCC_6H_4Cu	**7m**	p-$NCC_6H_4COOCH_3$	99 (40)
2o		**7o**		75 (59)
2p		**7p**		85 (65)

[a] Quantitative results were obtained by GC analyses. The first value represents the yield based upon the amount of organocopper (**2**) present just prior to the addition of CO_2. The second value (in parentheses) represents the overall yield from starting material (**1**).

simple S_N2 mechanism can explain many of the reactions, it obviously cannot account for the production of the *tert*-butyl ester. It is thought that the formation of sterically hindered esters proceeds through a radical mechanism.[2b,c]

The overall three-step synthetic process, consisting of the oxidative addition of activated copper to the functionalized aryl iodide followed by carboxylation and subsequent esterification, can be accomplished in moderate yields as illustrated in Table 3. This demonstrates the viability and utility of the process. The ease by which this one-pot procedure can be applied opens the door to a new synthesis of a variety of compounds. Some of these compounds have important applications such as methyl 2,4-difluorobenzoate (**2p**), which is an intermediate in the syntheses of novel antifungal derivatives.[24]

Preliminary Studies of Ester Synthesis Utilizing Alkyl Chloroformates. An alternative pathway to the reported ester synthesis would be the reaction of functionalized organocopper reagents with organo chloroformates. We have begun preliminary work to explore the feasibility of this approach by examining the reactions of 2-fluorophenylcopper and 2-chlorophenylcopper with methyl-, ethyl-, and isopropyl chloroformate. Ethyl 2-fluorobenzoate (**6b**) was produced in 54% yield, and isopropyl 2-fluorobenzoate (**6e**) in 10% yield. All other reactions produced yields below 10%. These reactions are still under active investigation.

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Conclusions

A useful and practical method for producing functionalized aryl acids and esters from the corresponding aryl iodides has been developed. The reaction conditions are gentle, yields are moderate to good, and the position of the entering carboxyl group is unambiguous. This approach compliments existing methods for producing aryl acids and esters and, in many cases, offers definite advantages in terms of the scope of application and conditions of reaction.

Experimental Section

Starting Materials. All starting materials were commercially purchased as reagent grade or better and used as received unless otherwise stated below.

4-Iodobenzophenone (1n)[13b,25] and **Methyl 2-Iodobenzoate (1i).**[13c,26] Both of these compounds were previously synthesized in bulk in our laboratory by published procedures. The purity of the compounds was established by ^{1}H NMR.

Methyl 3-Iodobenzoate (1j). This compound was synthesized[27] by heating 3-iodobenzoic acid in an excess of methanol containing a catalytic amount of H_2SO_4 to produce a solid (4.40 g, 16.8 mmol, 80% yield). The literature IR data[28] and ^{13}C NMR data[29] matched that of the sample. Purity was established by ^{13}C NMR.

Methyl 4-Iodobenzoate (1k). This compound was synthesized in a manner analogous to that for **1j** beginning with 4-iodobenzoic acid to produce a solid (4.51 g, 17.2 mmol, 82% yield). The literature mp,[30] IR data,[31] and ^{1}H NMR data[31] all matched that of the sample. Purity was established by ^{1}H NMR.

Formation of Activated Copper. 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 (0.076 g, 11 mmol, 1 equiv, small chips from lithium rod, Aldrich) and either naphthalene or biphenyl (12 mmol, 1.1 equiv) 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, no chips of Li remaining) a mixture of $CuI \cdot P(Et)_3$[32] (3.09 g, 10 mmol, 0.91 equiv) 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.

Synthesis of Functionalized Aryl Acids (4a−p). The functionalized aryl iodide or bromide starting material (**1a**−**p**) was added (5 mmol, 0.5 equiv) to the activated copper solution along with an internal standard (typically decane, 0.40 mL, 2.05 mmol). First, the internal standard was injected into the solution neat. Liquid starting materials were then injected neat, or solid starting materials were dissolved in THF (5 mL) and then injected via syringe. The solution was stirred for 30 min, after which an aliquot (0.5 mL) of the solution was removed, quenched with a few drops of 0.1 M HCl, and and analyzed by gas chromatography using the internal standard method to obtain the yield of organocopper intermediate (**2a**−**p**). Carbon dioxide (gas cylinder) was then bubbled through the reaction mixture for 30 min, after which the solution was allowed to stir for 24 h under an atmosphere of CO_2. At this point the functionalized copper benzoate (**3**) was either esterified or converted to the acid and isolated. The functionalized aryl acid was isolated by acidifying the contents of the reaction flask with 1 M HCl followed by filtration to remove the insoluble salts. The solution was extracted with ethyl ether (3 × 10 mL), and the aqueous layer discarded. In turn, the ether solution was extracted with saturated $NaHCO_3$ (3 × 10 mL). The aqueous solution was acidified with 1 M HCl and extracted with ether (3 × 10 mL). The ether solution was then dried over $MgSO_4$, after which the ether was removed by rotary evaporation to reveal the functionalized aryl acid. Quantitation was based upon the isolated yield. The acids were characterized by comparing their spectral and physical properties to those of authentic commercial samples or to data reported in the literature. Purity was established by melting point and also by HPLC. All acids synthesized in this work have been previously reported, and most are commercially available.

Synthesis of Functionalized Aryl Esters (6, 7). To the reaction flask containing the previously formed functionalized copper benzoate (**3**) is added 15 mL of a dipolar aprotic solvent (DMF or DMSO) followed by an excess (15 mmol, 3 equiv, neat) of the desired alkyl halide (5). The reaction is heated to reflux (typically 70 °C for THF solutions and 85 °C for DME solutions) for 5 h to produce the ester. To isolate the ester, the contents of the reaction flask (typically 45 mL) were poured into HCl (0.1 M, 50 mL). Ethyl ether was added (25 mL), and the layers were separated. The organic layer was washed twice with saturated $NaHCO_3$ (25 mL) and once with water and dried over $MgSO_4$. The ester was isolated by flash chromatography after separating the more volatile compounds by rotary evaporation. The esters were characterized by their spectral and physical properties. The majority of the esters synthesized in this work have been previously reported, and most are commercially available. For newly reported compounds, NMR, IR, LRMS, and physical properties have been provided as Supporting Information. Quantitation and the purity of the esters were determined by gas chromatography using the internal standard method. Authentic samples of the esters were used to establish response factors.

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Supporting Information Available: Spectroscopic and physical data used to characterize previously reported compounds are referenced. For newly reported compounds, NMR, IR, LRMS, and physical data have been provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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