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Copper-Catalyzed Sequential Alkyl/Aryl or Vinyl Esterification of Dicarboxylic Acid Anhydrides with Alkoxysilanes

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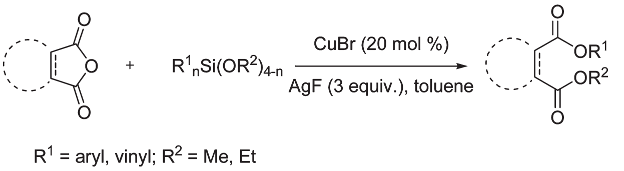
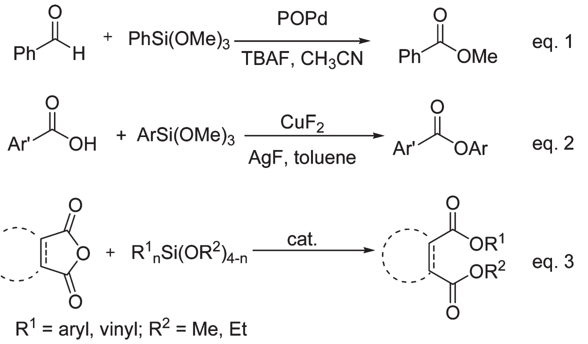


A copper(I)-catalyzed bis-esterification of cyclic anhydrides with aryl and vinyl alkoxysilanes is described, in which the alkoxy and aryl (or vinyl) esters of dicarboxylic acids were prepared in one pot with moderate to good yields. Notably, vinyl trimethoxysilanes also worked well with this procedure.

Aryl trialkoxysilanes have been widely used as significant transmetalation reagents for the formation of C$-$C,[1,2] C$-$N,[3] and C$-$S bonds[4] because of their low cost, easy availability, nontoxic byproducts, and stability under many reaction conditions. However, in these reactions, only the aryl moiety of aryl trialkoxysilane has been transferred to the organic product and the alkoxyl moiety was discarded as waste, which diminishes the atom-economy for such transformations. In 2006, Lerebours and Wolf reported that the methoxy of phenyltrimethoxysilane was transferred to aldehyde to form methyl benzoate (Scheme 1, eq 1).[5] However, to the best of our knowledge, examples of the transfers of both the aryl and alkoxy moieties of the aryl trialkoxysilane have never been reported. Recently, we developed a copper(II)-catalyzed aromatic esterification reaction of carboxylic acid with aryl and vinyl trialkoxysilanes (Scheme 1, eq 2).[6] As part of our continuing interest in the application of aryl trialkoxysilanes[3a,7] and aryl trialkoxysilanes-mediated C$-$O bond-forming reactions, we herein report a bis-esterification of cyclic anhydrides with aryl trialkoxysilanes and vinyl trialkoxysilanes, in which the alkoxy and aryl (or vinyl) esters of dicarboxylic acids are prepared in one pot (Scheme 1, eq 3).

SCHEME 1. The Esterification Reaction with Aryl Trimethoxysilane



Initial studies were performed by using the reaction of phthalic anhydride with phenyl trimethoxysilane as the model reaction, employing $Cu(OAc)_2$ as the catalyst at 130 °C (Table 1). Considering that the C$-$Si bond generally needs a fluoro source for activation, we first focused on fluoro source screening and found that AgF showed good activity (Table 1, entry 6). A profound solvent effect was observed and nonpolar toluene was found to be superior to other solvents. The source of copper in the reactions also had dramatic effects on the reaction. CuBr was the best reagent, leading to 87% isolated yield of the desired product (Table 1, entry 11). In addition, GC-MS was conducted when using $Cu(OAc)_2$

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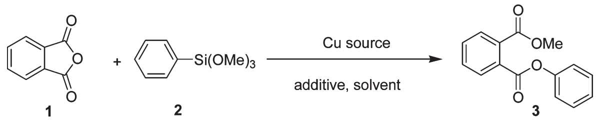
TABLE 1. Selected Results of Screening the Optimal Conditions[a]

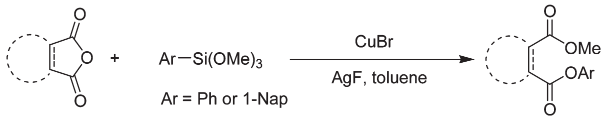


1 2 3

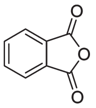
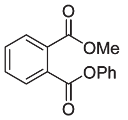
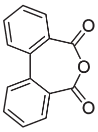
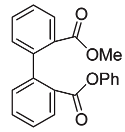
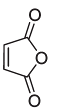
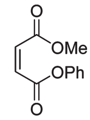
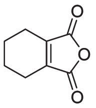
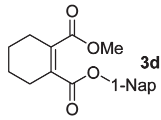
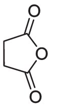
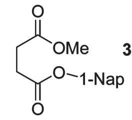
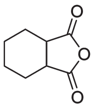
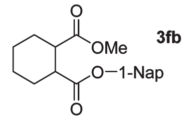
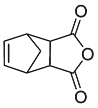
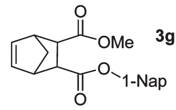
entry	Cu source	additive	solvent	yield (%)
1	$Cu(OAc)_2$	$TBAF\cdot3H_2O$	toluene	< 5
2	$Cu(OAc)_2$	KF	toluene	< 5
3	$Cu(OAc)_2$	CsF	toluene	< 5
4	$Cu(OAc)_2$	FeF_3	toluene	10
5	$Cu(OAc)_2$	CuF_2	toluene	< 5
6	$Cu(OAc)_2$	AgF	toluene	55
7	$Cu(OAc)_2$	AgF	DMSO	30
8	$Cu(OAc)_2$	AgF	NMP	20
9	$Cu(OAc)_2$	AgF	$ClCH_2CH_2Cl$	40[b]
10	$Cu(OAc)_2$	AgF	CH_3CN	15[b]
11	CuBr	AgF	toluene	87
12	$CuBr_2$	AgF	toluene	39
13	$CuSO_4$	AgF	toluene	50
14	$Cu(acac)_2$	AgF	toluene	58
15	Cu_2O	AgF	toluene	85
16	CuO	AgF	toluene	8
17	CuI	AgF	toluene	63
18	CuF_2	AgF	toluene	67
19	CuCl	AgF	toluene	47
20		AgF	toluene	0

[a] Reaction conditions: phthalic anhydride **1** (0.2 mmol), $PhSi(OMe)_3$ **2** (0.3 mmol), Cu source (20 mol %), additive (3 equiv), dry solvent (2 mL), 130 °C, 30 h. [b] 80 °C

TABLE 2. Copper(I)-Catalyzed Esterification Reaction of Anhydride with Phenyl and Napthalenyl Trimethoxysilanes[a]



1 2a or 2b 3

entry	substrate 1	product 3	yield (%)
1	 **1a**	 **3aa**	87
2	 **1b**	 **3ba**	75
3	 **1c**	 **3ca**	65
4	 **1d**	 **3db**	70
5	 **1e**	 **3eb**	78
6	 **1f**	 **3fb**	63
7	 **1g**	 **3gb**	42

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), CuBr (20 mol %), AgF (3 equiv), dry toluene (2 mL), 130 °C, 30 h.

as catalyst. No acetyloxylation product was detected. The blank experiment confirmed that in the absence of the copper salts, no desired product was formed (Table 1, entry 20). A compatible yield was obtained when the process was conducted under an inert atmosphere or oxygen. The result shows that oxygen is not required for this transformation.

Encouraged by these results, we further pursued the scope of the process with respect to the other substrates. As expected, a series of anhydrides worked well under the reaction conditions (Table 2). Arene dicarboxylic acid anhydrides coupled efficiently with phenyl trimethoxysilane, and good yields were obtained (Table 2, entries 1 and 2). It is worth noting that aliphatic and unsaturated dicarboxylic acid anhydrides were also good reaction partners (Table 2, entries 3−7). However, steric hindrance of dicarboxylic acid anhydrides had little effect on the reaction. For example, **3gb** was isolated in 42% yield (Table 2, entry 7). Homophthalic anhydride was subjected to the standard reaction conditions. However, a complex mixture was obtained. Importantly, the rigorous exclusion of air/moisture was not required in any of these transformations, a condition that represents an exceedingly practical alternative method for the synthesis of esters. When this reaction was conducted on a 1 mmol scale, the desired product **3aa** was formed in a satisfactory 72% yield.

Having demonstrated the utility of the optimized conditions on phenyl and 1-naphthalenyl trimethoxysilanes, we turned our attention to the scope of aryl trimethoxysilanes. As expected, a series of aryl alkoxysilanes reacted smoothly, providing esters in moderate to good yields (Table 3). It is worth pointing out that vinyl was tolerated under the standard procedure. As far as **2f** and **2g** were concerned, both the vinyl and alkoxy moieties were transferred to the product, while the methyl moiety remained untouched (Table 3, entries 5 and 6). The direct addition of carboxylic acids to terminal alkynes catalyzed by Hg,[8] Ru,[9] Rh,[10] or Ir[11] is a straightforward and atom-economical process for the synthesis of enol esters. However, the use of toxic mercury salts or expensive catalysts has greatly diminished the scope of the aforementioned procedure. Thus, our procedure represents a practical alternative method to access vinyl esters.

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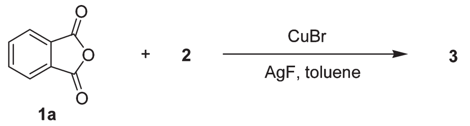
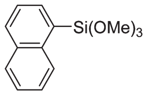
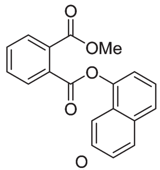
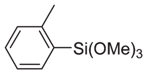
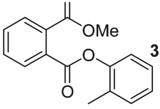
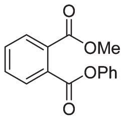
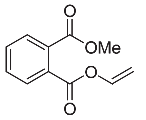
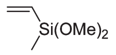
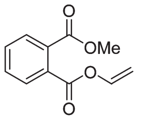
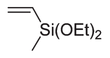
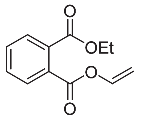
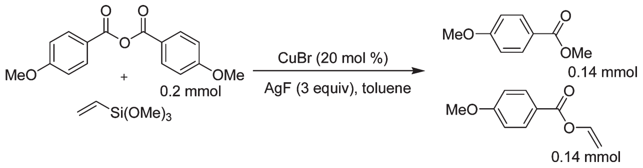
TABLE 3. Copper(I)-Catalyzed Esterification Reaction of Phthalic Anhydride with Aryl and Vinyl Trimethoxysilane[a]



entry	substrate **2**	product **3**	yield (%)
1	 **2b**	 **3ab**	80
2	 **2c**	 **3ac**	79
3	$Ph_2Si(OMe)_2$ **2d**	 **3ad**	78
4	 **2e**	 **3ae**	65
5	 **2f**	 **3af**	67
6	 **2g**	 **3ag**	60

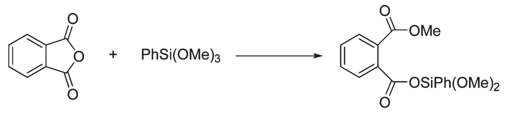
[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), CuBr (20 mol %), AgF (3 equiv), dry toluene (2 mL), 130 °C, 30 h.

SCHEME 2. Reaction of Acyclic Anhydride with Vinyl Trimethoxysilane



The acyclic anhydride 4-methoxy benzoic anhydride and vinyl trimethoxysilane were subjected to the procedure, and methyl 4-methoxybenzoate and vinyl 4-methoxybenzoate were isolated in equal amounts (Scheme 2).

Under the standard reaction condition, the formation of methyl 4-methoxybenzoate was confirmed by GC-MS in the absence of CuBr. The silyl carboxylate **A**, which derived from the reaction of anhydride and silicon alkoxide (Figure 1),[12] may be the key intermediate for this transformation.



A

FIGURE 1. Plausible intermediate.

In conclusion, we have developed a novel esterification of dicarboxylic acid anhydrides with the readily prepared aryl and vinyl trimethoxysilanes. The procedure transfers both alkoxyl and aryl moieties to the esterification products in one pot, and represents a novel and atom-economical method for the synthesis of dicarboxylic esters.

Experimental Section

General Procedure for the Esterification Reaction of Anhydride with Trialkoxysilane. Under air, a sealed tube was charged with anhydride (0.2 mmol), silane reagent (0.3 mmol), CuBr (5.7 mg, 20 mol %), AgF (75.5 mg, 0.6 mmol), and dry toluene (2 mL). The mixture was stirred at 130 °C. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the desired product.

Methyl naphthalen-1-yl phthalate (3ab): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10−8.00 (m, 2H), 7.91−7.89 (m, 3H), 7.86−7.79 (m, 2H), 7.69−7.52 (m, 4H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.9, 165.9, 146.8, 134.7, 132.6, 131.8, 131.3, 131.2, 129.4, 129.2, 128.0, 126.8, 126.53, 126.50, 126.2, 125.5, 121.3, 117.9, 52.8; IR (prism, cm^{-1}) ν 2930, 2159, 1727, 1223, 1110, 1054; HRMS (EI) calcd for $C_{19}H_{15}O_4$ $(M + H)^+$ 307.0970, found 307.0962.

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Supporting Information Available: Experimental procedures along with copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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