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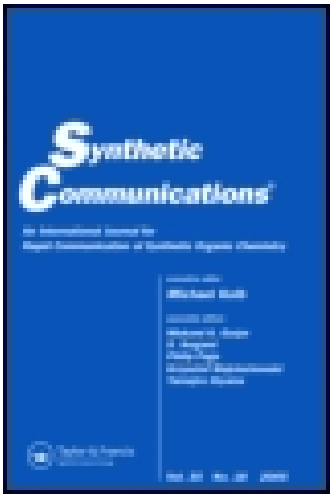

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Two New Catalysts for the Dehydrogenative Coupling Reaction of Carboxylic Acids with Silanes—Convenient Methods for an Atom-Economical Preparation of Silyl Esters

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Two New Catalysts for the Dehydrogenative Coupling Reaction of Carboxylic Acids with Silanes—Convenient Methods for an Atom-Economical Preparation of Silyl Esters

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Abstract: Tris(triphenylphosphine)cuprous chloride [$Cu(PPh_3)_3Cl$] has been found to be an efficient catalyst for the dehydrosilylation of carboxylic acids with silanes. In the presence of 4 mol% $Cu(PPh_3)_3Cl$, dehydrosilylation reactions in acetonitrile afforded the corresponding silyl esters at 80°C in good yields. It was noted that triphenylphosphine itself also functions as an adequate catalyst for the reaction.

Keywords: catalysts, dehydrosilylation, silyl esters, triphenylphosphine, tris(triphenylphosphine)cuprous chloride

INTRODUCTION

Silyl esters are key intermediates for the preparation of functional polymeric substrates such as easily degradable poly(silyl ester)s, widely utilized as recyclable materials, gene delivery carriers, matrices for drug delivery, and biodegradable surgical devices.[1] In this respect, unsaturated silyl esters are important substrates in polymerization reactions. Much attention has been

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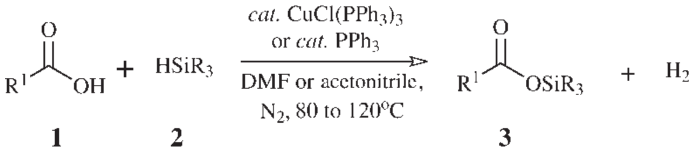
devoted to the development of a simple, practical, and atom-economical preparation of stable and easily isolable silyl esters.

A conventional way to prepare silyl esters is the coupling reaction of carboxylic acids and chlorosilanes.[2] Hydrogen chloride is unavoidably produced in these procedures, and a stoichiometric or even excess amount of base such as amines or ammonia is needed to neutralize the HCl gas formed. As chlorosilanes themselves are made by the chlorination of silanes, either with chlorine gas[1g] or with hydrochloric acid under Pd/C catalysis,[3] the synthesis of silyl esters from the corresponding silanes necessitates two reaction steps. Although a number of newer synthetic methods for silyl esters have appeared and a lot of literature concerns itself with the transition-metal-catalyzed coupling of OH-containing compounds such as water and alcohols with silanes,[4] there are still few examples of the dehydrogenative coupling reaction of carboxylic acids with silanes. The reported dehydrosilylation reactions are exclusively catalyzed by metal salts such as zinc chloride or, more frequently, by transition metals and metal complexes such as [$(Ph_3P)CuH$], H_2PtCl_6, Rh, and Pd.[5] Transition metals are expensive. Catalysts such as [$(Ph_3P)CuH$] require a multiple-step synthesis and are very difficult to obtain in high purity. Moreover, transition-metal-catalyzed coupling of unsaturated carboxylic acids and silanes always results in the formation of by-products because of the known ability of Rh, Pd, and Pd/C to act as hydrogenation catalyst in the reduction of carbon–carbon double bonds in the desired olefinic silyl esters, leading to troublesome purification. Because of this, the screening of catalysts for this reaction remains of interest.

Here, we report that both tris(triphenylphosphine)cuprous chloride [$Cu(PPh_3)_3Cl$] and triphenylphosphine (Ph_3P) catalyze the dehydrogenative coupling of carboxylic acids with silanes, yielding the corresponding silyl esters selectively, without formation of any reduced by-products in the case of unsaturated silyl esters (Scheme 1).

RESULTS AND DISCUSSION

In the presence of 4 mol% $Cu(PPh_3)_3Cl$, the reaction was carried out in acetonitrile by heating a mixture of the corresponding acid (**1**) and silane (**2**) at 80°C



Scheme 1.

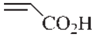
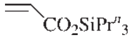
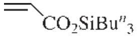
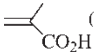
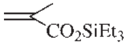
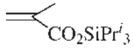
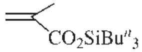
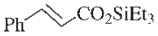
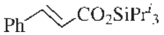
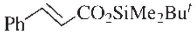
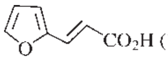
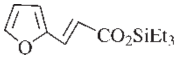
under an N_2 atmosphere (Table 1). To optimize the reaction conditions, the coupling was performed with acetic acid (**1a**) and triethylsilane (**2a**) as substrates under different reaction conditions. The desired coupling was found to be complete after 4 h at 80°C (4 mol% catalyst), affording the corresponding triethylsilyl acetate (**3a**) in 90% yield (Table 1, run 1). Using $Cu(PPh_3)_3Cl$ as catalyst, the reaction time for the transformation is much shorter than when using $ZnCl_2$.[5g] The use of additional $Cu(PPh_3)_3Cl$ (e.g., 8 mol%) did not accelerate the reaction further, however. On the other hand, a decrease of the amount of catalyst (to 2 mol%) led to a decrease in reaction rate, where 39% of the triethylsilane (**2a**) (as determined by GC) remained unreacted even after the reaction mixture was heated for 12 h at 80°C. Also, the reaction temperature plays an important role. Thus, the transformation was slow when the reaction was carried out at 40°C or 60°C, and significant amounts of triethylsilane (**2a**) could still be detected after 48 h (78% at 40°C, 49% at 60°C, according to GC analysis). At room temperature, no coupling reaction was observed, and the triethylsilane (**2a**) remained unchanged. When the reaction was carried out in other solvents, such as in hexane (at 69°C), cyclohexane (at 80°C), 1,4-dioxane (at 100°C), or benzene (at 80°C), the reaction was found to be slower than in acetonitrile, where again triethylsilane (**2a**) remained unreacted after 24 h at reflux temperature of the corresponding solvent (45–78%, as estimated by GC analyses).

A wide range of trialkylsilanes (**2**) could be reacted successfully when using the optimized conditions discussed previousy [run 1: 4 mol% $Cu(PPh_3)_3Cl$, acetonitrile, 80°C]. The relative reactivity of the silanes is of the order Et_3SiH (**2a**) $>$ n-Pr_3SiH (**2b**) $>$ n-Bu_3SiH (**2c**) (Table 1, runs 1 and 2 vs. 3). Also benzoic acid (**1d**) and substituted benzoic acids (**1e–1g**) could be submitted to the reaction successfully (runs 7–14). It must be noted that under these conditions also unsaturated silyl esters such as acrylic (**1h**), methacrylic (**1i**), cinnamic (**1j**), and furylacrylic (**1k**) acids could be reacted, leading to the desired monomers of poly(silyl ester)s. Here, no hydrogenated by-products were formed, as is usually the case in many of the Pd-, Pt- and Ru-based catalysts.

Also, triphenylphosphine (PPh_3) itself was found to catalyze the dehydrogenative reactions of carboxylic acids with silanes. Thus, when a mixture of carboxylic acid (**1**), silane (**2**), and PPh_3 (4 mol%) in *N,N*-dimethylformamide (DMF) was heated under a nitrogen atmosphere at 120°C for 12–18 h, the desired silyl esters were obtained in good yield (Table 2, reaction monitored by GC). Again, the transformation of propionic acid (**1b**) with triethylsilane (**2a**) was used to optimize the reaction conditions. Here, the dehydrogenative coupling was found to be finished after 15 h at 120 ºC, in the presence of 4 mol% PPh_3, affording the corresponding triethylsilyl propionate (**3d**) in 87% yield (Table 1, run 3). As with using $Cu(PPh_3)_3Cl$, an increase of catalyst did not accelerate the reaction further, whereas a decrease in PPh_3 (to 1 or 2 mol%) slowed the reaction significantly, and 48% and 30% of

Table 1. $CuCl(Ph_3P)_3$-catalyzed dehydrocoupling of carboxylic acids and silanes[a]

Run	Acid	Silane	Time (h)	Product	Yield (%)[b]
1	CH_3CO_2H (**1a**)	Et_3SiH (**2a**)	4	$CH_3CO_2SiEt_3$ (**3a**)	90[5c]
2	**1a**	n-Pr_3SiH (**2b**)	4	$CH_3CO_2SiPr^n_3$ (**3b**)	88[6]
3	**1a**	n-Bu_3SiH (**2c**)	4	$CH_3CO_2SiBu^n_3$ (**3c**)	86[6]
4	$CH_3CH_2CO_2H$ (**1b**)	**2a**	4	$CH_3CH_2CO_2SiEt_3$ (**3d**)	84[7]
5	**1b**	**2c**	6	$CH_3CH_2CO_2SiBu^n_3$ (**3e**)	76[8]
6	$CH_3(CH_2)_8CO_2H$ (**1c**)	i-Pr_3SiH (**2d**)	7	$CH_3CH_2CO_2SiPr^i_3$ (**3f**)	79[9]
7	$C_6H_5CO_2H$ (**1d**)	**2b**	4	$C_6H_5CO_2SiPr^n_3$ (**3g**)	80[10]
8	**1d**	**2c**	6	$C_6H_5CO_2SiBu^n_3$ (**3h**)	81[11]
9	**1d**	**2d**	6	$C_6H_5CO_2SiPr^i_3$ (**3i**)	80[9]
10	**1d**	t-$BuMe_2SiH$ (**2e**)	6	$C_6H_5CO_2SiMe_2Bu^t$ (**3j**)	85[9]
11	3-$BrC_6H_4CO_2H$ (**1e**)	**2d**	6	3-$BrC_6H_4CO_2SiPr^i_3$ (**3k**)	84[12]
12	**1e**	**2e**	7	3-$BrC_6H_4CO_2SiMe_2Bu^t$ (**3L**)	82[12]
13	3-$ClC_6H_4CO_2H$ (**1f**)	**2e**	7	3-$ClC_6H_4CO_2SiMe_2Bu^t$ (**3m**)	81[12]

14	4-$O_2NC_6H_4CO_2H$ **(1g)**	**2e**	8	4-$O_2NC_6H_4CO_2SiMe_2Bu^t$ **(3n)**	79[13]
15	 **(1h)**	**2a**	5	 **(3o)**	83[14]
16	**1h**	**2b**	5	 **(3p)**	78[15]
17	**1h**	**2c**	6	 **(3q)**	74[16]
18	 **(1i)**	**2a**	5	 **(3r)**	83[17]
19	**1i**	**2d**	6	 **(3s)**	76[15]
20	**1i**	**2c**	6	 **(3t)**	79[5b]
21	 **(1j)**	**2a**	5	 **(3u)**	87[18]
22	**1j**	**2d**	6	 **(3v)**	81[18]
23	**1j**	**2e**	8	 **(3w)**	72[12]
24	 **(1k)**	**2a**	6	 **(3x)**	86[19]

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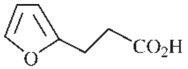
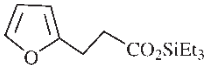
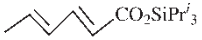
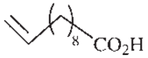
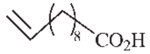
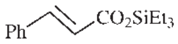
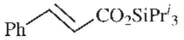
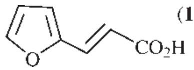
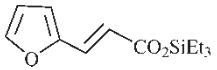
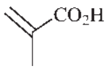
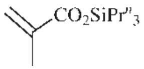
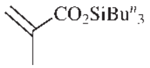
[a] Carboxylic acid (20 mmol), silane (20 mmol), $CuCl(PPh_3)_3$ (0.8 mmol, 4 mol%).

[b] Isolated yield.

Table 2. Ph_3P-catalyzed dehydrocoupling of carboxylic acids with silanes[a]

Run	Acid	Silane	Time (h)	Product	Yield (%)[b]
1	CH_3CO_2H (**1a**)	Et_3SiH (**2a**)	12	$CH_3CO_2SiEt_3$ (**3a**)	91[5c]
2	**1a**	n-Pr_3SiH (**2b**)	12	$CH_3CO_2SiPr^n_3$ (**3b**)	88[6]
3	**1a**	n-Bu_3SiH (**2c**)	14	$CH_3CO_2SiBu^n_3$ (**3c**)	86[6]
4	$CH_3CH_2CO_2H$ (**1b**)	**2a**	15	$CH_3CH_2CO_2SiEt_3$ (**3d**)	84[7]
5	**1b**	**2c**	14	$CH_3CH_2CO_2SiBu^n_3$ (**3e**)	76[8]
6	**1b**	**2b**	14	$CH_3CH_2CO_2SiPr^n_3$ (**3-I**)	85[6]
7	$CH_3(CH_2)_8CO_2H$ (**1c**)	i-Pr_3SiH (**2d**)	15	$CH_3(CH_2)_8CO_2SiPr^i_3$ (**3f**)	79[9]
8	$C_6H_5CO_2H$ (**1d**)	**2d**	14	$C_6H_5CO_2SiPr^i_3$ (**3i**)	83[9]
9	**1d**	t-$BuMe_2SiH$ (**2e**)	16	$C_6H_5CO_2SiMe_2Bu^t$ (**3j**)	77[9]
10	3-$BrC_6H_4CO_2H$ (**1e**)	**2d**	15	3-$BrC_6H_4CO_2SiPr^i_3$ (**3k**)	80[12]
11	3-$ClC_6H_4CO_2H$ (**1f**)	**2d**	14	3-$ClC_6H_4CO_2SiPr^i_3$ (**3y**)	81[12]
12	3-$ClC_6H_4CO_2H$ (**1f**)	**2e**	18	3-$ClC_6H_4CO_2SiMe_2Bu^t$ (**3j**)	77[12]
13	4-$ClC_6H_4CO_2H$ (**IL**)	**2a**	13	4-$ClC_6H_4CO_2SiEt_3$ (**3z**)	85[20]
14	4-$O_2NC_6H_4CO_2H$ (**1g**)	**2e**	18	4-$O_2NC_6H_4CO_2SiMe_2Bu^t$ (**3n**)	75[13]
15	$C_6H_5CH_2CO_2H$ (**1m**)	**2a**	14	$C_6H_5CO_2SiEt_3$ (**3o**)	80[7]

16	 **(1n)**	**2a**	12	 **(3-II)**	79[19]
17	 **(1o)**	**2d**	14	 **(3-III)**	78[9]
18	 **(1p)**	**2d**	14	 **(3-IV)**	74[12]
19	 **(1j)**	**2a**	13	 **(3u)**	82[18]
20	**1j**	**2d**	15	 **(3v)**	75[18]
21	 **(1k)**	**2a**	13	 **(3x)**	80[19]
22	 **(1i)**	**2b**	14	 **(3s)**	86[21]
23	**1i**	**2c**	15	 **(3t)**	78[5c]

[a] Carbolic acid (20 mmol), silane (20 mmol), PPh$_3$ (0.8 mmol, 4 mol%).

[b] Isolated yield.

Et_3SiH (**2a**) (GC ratio) was found to remain unreacted after 48 h at 120°C. Also, the reaction progressed more slowly when carried out at 80°C or 100°C, with 72% of the triethylsilane (**2a**) remaining unreacted at 80°C and 51% at 100°C after 48 h. Solvents other than DMF, such as xylene and anisole, were studied but found to be inadequate, as even after 72 h at 120°C significant amounts of triethylsilane (**2a**) remained unreacted (62% and 86%, respectively). Phosphines other than triphenylphosphine were also tested as catalysts, such as tri-*n*-butylphosphine, tri-*tert*-butylphosphine, tricyclohexylphosphine, tris(2-methylphenyl)phosphine, and 1,2-bis(diphenylphosphino)-ethane (all at 4 mol%, DMF, 120°C), but triphenylphosphine was found to give the best results.

As with $Cu(PPh_3)_3Cl$, the use of PPh_3 as catalyst allowed the transformation of a large number of substrates, both of silanes such as *n*-Pr_3SiH (**2b**), *n*-Bu_3SiH (**2c**), and *t*-$BuMe_2SiH$ (**2e**) and of acids such as benzoic acid (**1d**) or substituted benzoic acids (**1e–1g**, **1l**) (all reactions run with 4 mol% PPh_3, DMF, 120°C). Again, the desired unsaturated silyl esters could be obtained by dehydrogenative coupling reaction of the silanes with cinnamic acid (**1j**), furylacrylic acid (**1k**), 2,4-hexadienoic acid (**1o**), and methacrylic acid (**1i**). In none of the cases was the formation of overreduced by-products observed (Table 2, runs 16–23).

From these results, it can be seen that although both $Cu(PPh_3)_3Cl$ and PPh_3 can be used as catalyst in the dehydrogenative preparation of silyl esters, PPh_3 necessitates higher reaction temperatures and longer reaction times, where the product yields are comparable to those with $Cu(PPh_3)_3Cl$ as catalyst. Also, CuCl (at 4 mol% or 20 mol%) was examined as a catalyst for the reaction but was found to be less reactive, leaving 78% (at 4 mol%) and 56% (at 20 mol%) triethylsilane (**2a**) unreacted after 12 h in refluxing acetonitrile.

CONCLUSION

$Cu(PPh_3)_3Cl$ as well as PPh_3 are efficient catalysts for the dehydrogenative coupling of carboxylic acids (**1**) with silanes (**2**), where the corresponding silyl esters (**3**) are formed in good yields. No overreduction occurs when reacting bromo- (**1e**), chloro- (**1f** and **1L**), or nitrobenzoic (**1g**) acids with silanes (**2**) under the conditions. Especially interesting is the transformation of unsaturated carboxylic acids under this protocol, leading to unsaturated silyl esters, where no hydrogenation products are observed. This type of dehydrogenative coupling reaction of carboxylic acids with silanes provides another important example of a one-step, highly selective, atom-economical, and efficient synthetic method, which in the case of using PPh_3 can also be run under metal-free conditions. Further work on silylation of carboxylic acids is in progress in our laboratory.

EXPERIMENTAL

Typical Procedure with $Cu(PPh_3)_3Cl$ as Catalyst

To a mixture of propionic acid (**1b**) (40 mmol, 2.96 g) and triethylsilane (**2a**) (40 mmol, 4.64 g), $Cu(PPh_3)_3Cl$ (0.8 mmol, 710 mg, 0.04 eq.) was added at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at 80°C for 4 h. The desired triethylsilyl propionate (**3d**) was obtained as a colorless oil (yield: 84%) after distillation under reduced pressure (Table 1, run 4).

Typical Procedure with PPh_3 as Catalyst

To a mixture of propionic acid (**1b**) (40 mmol, 2.96 g) and triethylsilane (**2a**) (40 mmol, 4.64 g) in DMF (20 ml), triphenylphosphine (1.6 mmol, 0.42 g, 0.04 eq) was added at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at 120°C for 15 h (monitored by GC). The desired triethylsilyl propionate (**3d**) was obtained (yield: 87%) after distillation under reduced pressure (Table 2, run 3).

Triethylsilyl Propionate (3d)[7]

IR (neat): 684, 740, 824, 998, 1062, 1241, 1410, 1464, 1714, 2870, 2954 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.72 (6H, q, ^3J 7.8 Hz), 0.95 (9H, t, ^3J 7.8 Hz), 1.14 (3H, t, ^3J 7.6 Hz), 2.36 (2H, q, ^3J 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.42, 6.46, 9.34, 28.46, 175.20.

All of the silyl esters are known compounds and were compared with authentic samples [prepared by coupling of carboxylic acids and chlorosilanes in the presence of a base such as triethylamine or imidazole (*t*-butylsilyl esters) in dichloromethane] and were identified on the basis of their IR, ^1H NMR, ^{13}C NMR, and GC-MS spectral data.

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