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Pd-Catalyzed New Type of Cross-Coupling of RCOOH and Styryltrifluoroborates

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Abstract

The Palladium inserted hydridopalladium species represents as RCOOPdH. This work finds an interesting coupling of palladium inserted RCOOPdH species with potassium styryltrifluoroborates to synthesize new kinds of styryl ester compounds. $Pd(OAc)_2$ was most effective catalyst for this new cross-coupling reaction under microwave irradiation and gave styryl esters in good to moderate yields.

Keywords

Styryl Ester, Microwave, $Pd(OAc)_2$ as Catalyst, Microwave Heating

1. Introduction

Palladium inserted hydridopalladium species represents as RCOOPdH. Trost exhibited excellent atom economy chemistry by adding palladium inserted acetic acid to propargyl type alkynes [1]. Dixneuf reported ruthenium-catalyzed anti-Markovnikov trans addition of carboxylic acids to terminal alkynes [2]. Watanabe also reported ruthenium-catalyzed addition of carboxylic acids to alkynes in Markovnikov fashion [3]. In our early study, we also reported palladium inserted carboxylic acids addition to allenes [4]. There is no known cross coupling chemistry involving RCOOPdH species and potassium styryltrifluoroborates. In this work, we focus on to cross-coupling reaction of palladium inserted carboxylic acids with potassium styryltrifluoroborates to synthesize new kinds of styrylcarboxylate compounds (**Figure 1**). Esters observe in the building block of life, animal cells. Some common esterification techniques including Fischer esterification, Yamaguchi esterification are available in the literature [5]. In our study, we explore unprecedented approach for the synthesis of styryl carboxylate, not formed by typical ester processes. The study focuses on how to create

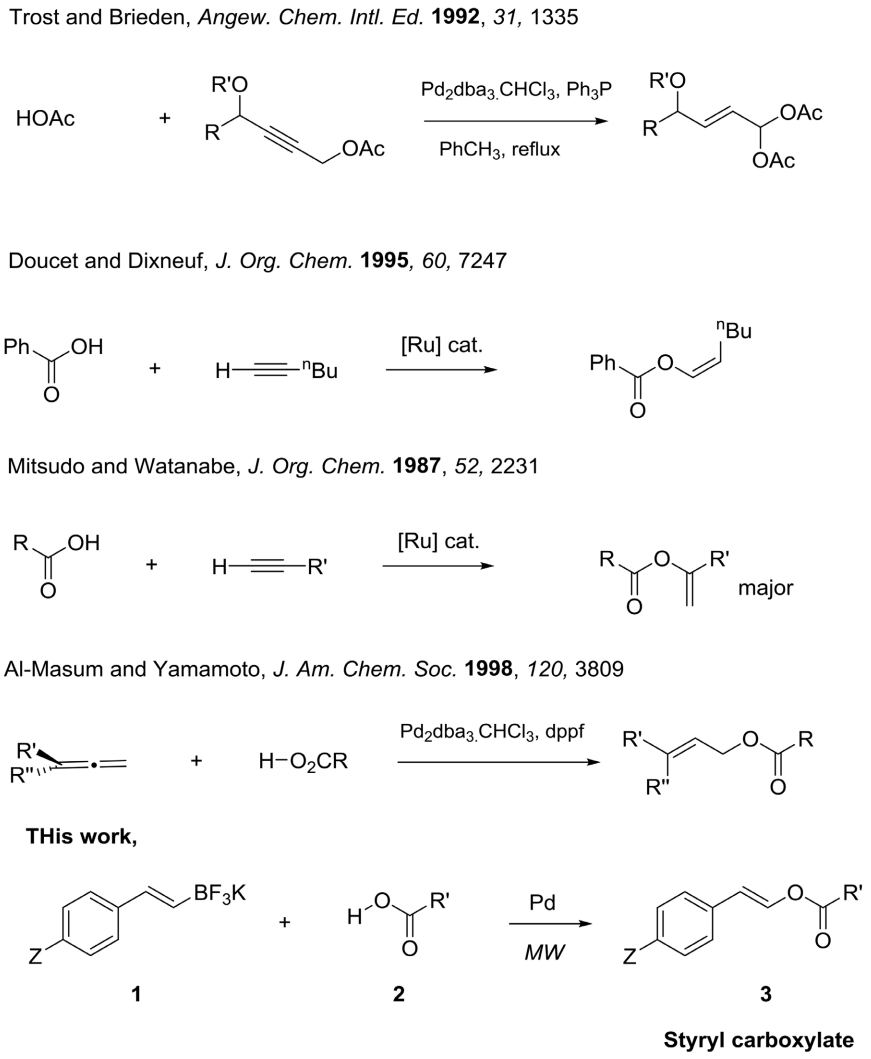

Figure 1. Unprecedented styryl caraboxylate.

RCOOPdH species and secure cross-coupling chemistry with potassium styryltrifluoroborates. The predicted styryl ester products have tremendous potential in synthetic organic chemistry and polymer chemistry. Vinyl acetate is a common ingredient found in coating world. It is widely used in the making of resins and polymers for adhesives, coatings and paints [6]. Large percentage of vinyl acetate is used for making polyvinyl acetate which is mainly used as adhesives in coating world. Polyvinyl alcohol is prepared from vinyl acetate, which has huge applications in adhesives, textiles, packaging firms. Vinyl acetate is also used in making vinyl chloride, vinyl copolymers [7].

The plausible reaction mechanism for the synthesis of styryl esters proposes in Figure 2.

2. Results

All experiments were performed by using a CEM discover microwave. Crude reaction mixtures analyzed by a Varian 3900 model GC-MS spectroscopy. Varian

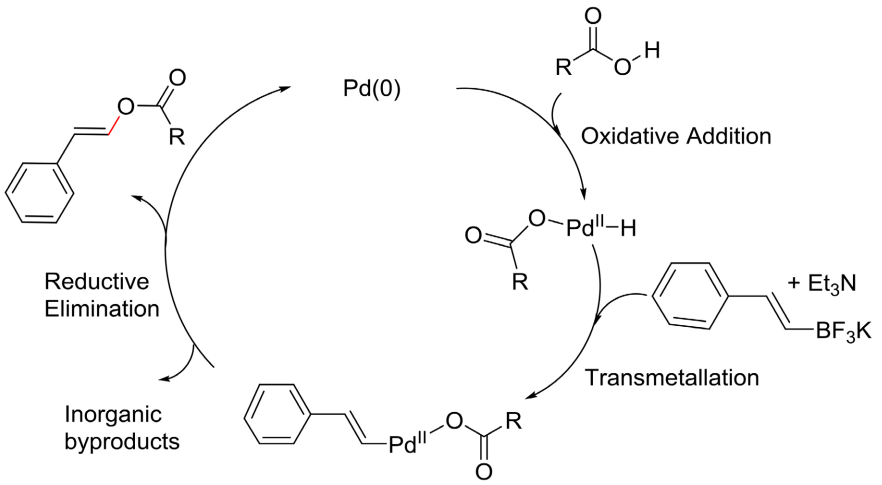

Figure 2. A plausible mechanism for cross-coupling of styrylBF$_3$K and carboxylic acid.

300 MHz NMR and Bruker 400 MHz NMR spectrometry were used to analyze ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra. Palladium catalyst purchases from Alfa Aesar and most of the reagents purchase from Sigma-Aldrich. Most of the solvents collect from Fischer Scientific and all dry solvents obtained from Sigma-Aldrich. All solvents are in pure form and ACS verified reagents.

Synthesis of Potassium Styryltrifluoroborates:

All potassium styryltrifluoroborates synthesize from the corresponding styrylboronoic acids by following a known synthetic procedure [8]. But we have modified this procedure several times in our lab to increase purity and percent yield. Synthesis of potassium styryltrifluoroborate from *trans*-2-(phenyl)-vinylboronic acid is a representative one.

First, in a 250-mL dry clean round bottom flask loaded with 2.96 g (20 mmol) of *trans*-2-(phenyl)-vinylboronic acid followed by 20 mL of methanol to obtain a clear solution. A saturated solution of 9.36 g (120 mmol) of KHF_2 and 30 mL of de-ionized water then transfer into clear boronic acid solution with vigorous stirring. The resulting mixture stirred for 4 h, which turned into thick suspension. The crude product concentrates under vacuum by using rotary evaporator. Then 250 mL of boiled acetone added into the solid product. KHF_2 is not soluble in acetone, but potassium styryltrifluoroborate easily dissolves in acetone. The filtrate collected and dried out the solvent completely by using rotary evaporator. For complete drying, the product connected to high-vacuum pump overnight. Finally, recrystallization process takes place to get a pure product. Minimum amount of acetone added to dissolve the solid product followed by adding diethyl ether. The recrystallized product dried under vacuum. White solid crystals collected and kept in sealed container. The container placed on the vacuum line overnight to remove trace solvents and obtain dry product. ^{1}H and ^{19}F confirmed the purity of the synthesized potassium styryltrifluoroborate (**Figure 3**).

Applying the same procedure, several other potassium styryltrifluoroborates also synthesized from corresponding boronic acids (**Table 1**).

Table 1. Synthesis of styryltrifluoroborates from boronic acid.

Styrylboronic acids as starting material	Synthesized Styryltrifluoroborates
trans-2-(4-fluorophenyl)-vinylboronic acid	Potassium *trans*-2-(4-fluorophenyl)-vinyltrifluoroborate
trans-2-(4-trifluoromethoxyphenyl)-vinylboronic acid	Potassium *trans*-2-(4-trifluoromethoxylphenyl)-vinyltrifluoroborate
trans-2-(4-trifluoromethylphenyl)-vinylboronic acid	Potassium *trans*-2-(4-trifluoromethylphenyl)-vinyltrifluoroborate
trans-2-(4-methylphenyl)-vinylboronic acid	Potassium *trans*-2-(4-methylphenyl)-vinyltrifluoroborate
trans-2-(4-chlorophenyl)-vinylboronic acid	Potassium *trans*-2-(4-chlorophenyl)-vinyltrifluoroborate

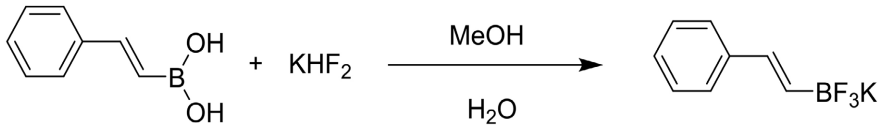

Figure 3. Synthesis of Potassium trans-2-(phenyl)-vinyltrifluoroborate.

For synthesizing potassium styryl esters from acids and potassium styryltrifluoroborates, we have worked on several factors to get a better result. These include using effective catalyst, appropriate solvent, base, different molar ratios of acid to styryltrifluoroborates, reaction time, temperature etc.

Optimized Reaction procedure for Synthesis of potassium Styryl Ester:

After attempting several reaction conditions, one equivalent of carboxylic acid and two equivalents of potassium styryltrifluoroborates found to be best for synthesizing styryl ester. The reaction scale is set at 0.25 mmol. In a dried reaction test tube, I, 20 mol % Pd (OAc) (0.011 g) added, capped, and flushed with argon to remove air. Using micro syringe, 0.25 mmol of carboxylic acid and 1 mL of THF added to the tube. The reaction tube placed into the CEM microwave and irradiated at 50˚C for 30 minutes. In another dry test tube II, 0.5 mmol of potassium styryltrifluoroborate added, capped and flushed with argon to remove air. By using syringe, 3 mL of acetone added to the tube to dissolve styryl trifluoroborates. Then, 1 mmol of triethyl amine (0.14 mL) added to the tube. Using a cannula, reaction mixture of tube II transferred to the reaction mixture of tube I and irradiated at 100˚C for another 30 minutes. The crude reaction product filtered through celite with ethyl acetate as eluent. To remove triethyl amine, we performed standard extraction using 30 mL of diethyl ether and 20 mL of ammonium chloride. We ran extraction two times and separated the top organic layer, dried over anhydrous Na_2SO_4. The organic layer filtered through celite with ethyl acetate as eluent to remove any unwanted impurities. The filtrate concentrated in rotary evaporator and the concentrated product dried overnight under vacuum pump for the complete removal of solvents.

Separation Techniques:

The crude reaction product mixture subjected to neutral alumina chromatography with hexane and hexane-dichloromethane (100:1) as eluents and collected the styryl ester product. The slurry of 40 mL (by volume) weight of alumina and eluent (Hexane: dichloromethane 100:1) transferred into the column,

tapped to remove air, and packed. The column is now ready to use for separation. 10 g of Al_2O_3 added to the crude reaction mixture and adsorbs the compound in alumina. After rotary evaporation, we got a fine powder, which transferred to the surface of the column. Solvent then added to the column and started collecting fractions in small Erlenmeyer flask. All collected fractions monitors by thin layer chromatography and identify the new spots for desired ester compound. We collected all those fractions with same Rf value in a clean and dry round bottom flask. The solvent evaporated and concentrated product analyzed by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Synthesis of Compound **3a**:

Synthesis of compound 3**a** as shown in Figure 4 is a representative one for the synthesis of styryl ester. ^{1}H NMR (chloroform-d6, 400 MHz): δ 7.41 (m, 2H, aromatic), 7.29 (m, 2H, aromatic), 7.21 (m, 1H, aromatic), 6.92 (d, J = 17.6 Hz, 1H, H_b), 6.64 (d, J = 15.2 Hz, 1H, H_a). ^{13}C NMR (chloroform-d6, 75.5 MHz): δ 167.74, 137.34, 132.80, 129.23, 128.64, 127.55, 126.36. Styryl ester **3a** obtained yielding 48 mg (90% yield).

Synthesis of Compound **3b**:

Synthesis of compound **3b** (as shown in Figure 5) is a representative one for the synthesis of styryl ester. ^{1}H NMR (chloroform-d6, 400 MHz): δ 7.30 (m, 2H, aromatic), 7.10 (m, 2H, aromatic), 6.82 (d, J = 17.3 Hz, 1H, H_b), 6.58 (d, J = 15.5 Hz, 1H, H_a), 2.32 (s, 3H, CH_3). ^{19}F NMR (Chloroform-d6, 300 MHz): δ −75. ^{13}C NMR (chloroform-d6, 300 MHz): δ 171.14, 137.35, 134.71, 132.25, 130.00, 129.36, 128.50, 126.24, 21.04. Styryl ester **3b** obtained yielding 38 mg (65% yield).

Synthesis of Compound **3c**:

Synthesis of compound **3c** (as shown in Figure 6) is a representative one for the synthesis of styryl ester. ^{1}H NMR (chloroform-d_6, 400 MHz): δ 7.49 (m, 2H, aromatic), 7.01 (m, 2H, aromatic), 6.75 (d, J = 15.3 Hz, 1H, H_b), 6.54 (d, J = 15.1

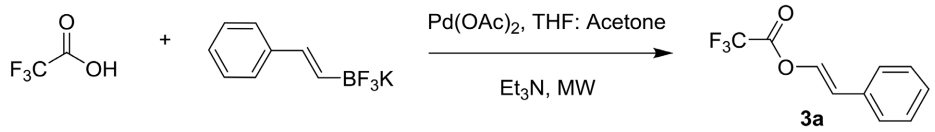

Figure 4. Synthesis of compound **3a**.

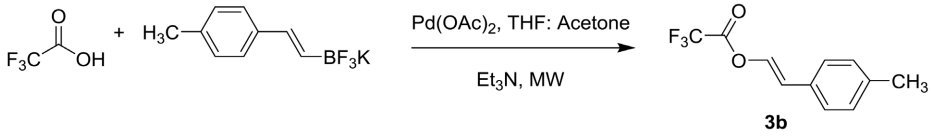

Figure 5. Synthesis of compound **3b**.

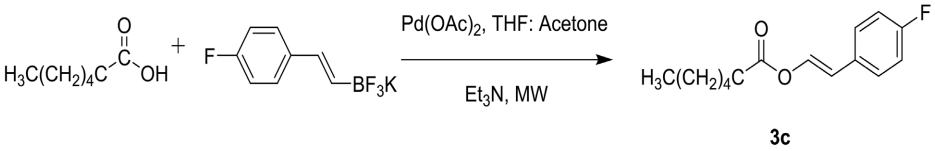

Figure 6. Synthesis of compound **3c**.

Hz, 1H, H_a), 2.11 (m, 3H, methylene), 21.12 (m, 8H, methylene). ^{19}F NMR (Chloroform-d_6, 400 MHz): δ −114. ^{13}C NMR (chloroform-d_6, 400 MHz): δ 163.54, 161.50, 132.40, 131.54, 128.80, 127.79, 115.74, 31.72, 30.32, 29.70, 29.27, 15.26. Styryl ester **3c** obtained yielding 40 mg (67% yield).

Synthesis of Compound **3d**:

Synthesis of compound **3d** (as shown in Figure 7) is a representative one for the synthesis of styryl ester. ^1H NMR (chloroform-d_6, 400 MHz): δ 7.55 (m, 2H, aromatic), 7.49 (m, 2H, aromatic), 6.98 (d, J = 18 Hz, 1H, H_b), 6.73 (d, J = 16.2 Hz, 1H, H_a), 2.14 (m, 2H, methylene), 1.38 (m, 9H, methylene). ^{19}F NMR (Chloroform-d_6, 300 MHz): δ −62.53. ^{13}C NMR (chloroform-d_6, 300 MHz): δ 167.76, 140.42, 132.68, 131.50, 130.97, 128.76, 126.59, 38.73, 30.36, 28.92, 23.74, 15.50. Styryl ester **3d** obtained yielding 38 mg (55% yield).

Synthesis of Compound **3e**:

Synthesis of compound **3e** (as shown in Figure 8) is a representative one for the synthesis of styryl ester. ^1H NMR (chloroform-d_6, 400 MHz): δ 7.30 (m, 2H, aromatic), 7.23 (m, 2H, aromatic), 7.21 (m, 1H, aromatic), 6.95 (d = 17.1 Hz, 1H, H_b), 6.63 (d, J = 16.9 Hz, 1H, H_a), 1.57 (m, 1H, methylene), 1.03 (m, 10H, methylene). Styryl ester **3e** obtained yielding 38 mg (70% yield).

Synthesis of Compound **3f**:

Synthesis of compound **3f** (as shown in Figure 9) is a representative one for the synthesis of styryl ester. ^1H NMR (chloroform-d_6, 400 MHz): δ 7.38 (m, 4 H, aromatic), 7.10 (m, 4H, aromatic), 6.69 (d, J = 18 Hz, 1H, H_b), 6.6.63 (d, J = 10.8 Hz, 1H, H_a), 5.71 (d, J = 17.6 Hz, 1H, H_b), 5.19 (d, J = 10.8 Hz, 1H, H_a), 2.34 (m, 6H, methylene), 1.43 (m, 1H, methylene), 1.25 (m, 2H, methylene), 0.90 (m, 1H, methylene). ^{13}C NMR (chloroform-d_6, 300 MHz): δ 171.13, 137.62, 134.86, 129.38, 126.27, 126.13, 112.75, 35.53, 29.73, 21.20, 13.50. Styryl ester **3e** obtained yielding 31 mg (60% yield).

Synthesis of Compound **3g**:

Synthesis of compound **3g** (as shown in Figure 10) is a representative one for the synthesis of styryl ester. ^1H NMR (chloroform-d_6, 300 MHz): δ 7.35 (m, 2H, aromatic), 7.02 (m, 2H, aromatic), 6.84 (d, J = 16.6Hz,1H, H_b), 6.58 (d, J = 16.4 Hz, 1H, H_a), 1.25 (m, 4H, methylene), 0.87 (m, 3H, methylene). ^{19}F NMR (Chloroform-d_6, 300 MHz): δ −114. ^{13}C NMR (chloroform-d_6, 300 MHz): δ 163.52, 161.06, 133.50, 131.52, 128.77, 127.78, 115.73, 31.58, 22.64, 14.10. Styryl ester **3g** obtained yielding 32 mg (62% yield).

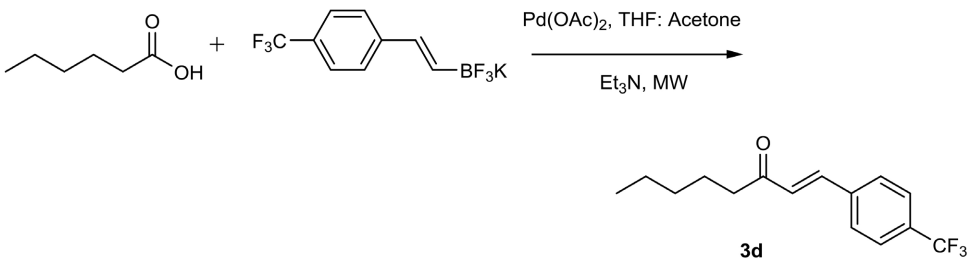

Figure 7. Synthesis of compound **3d**.

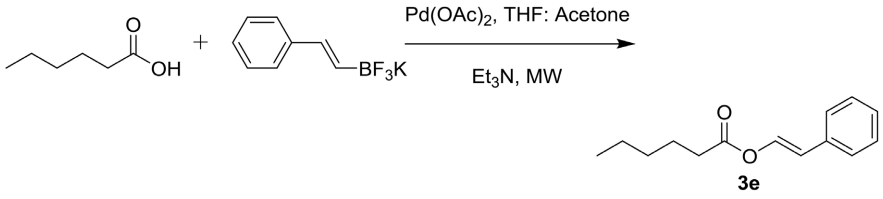

Figure 8. Synthesis of compound **3e**.

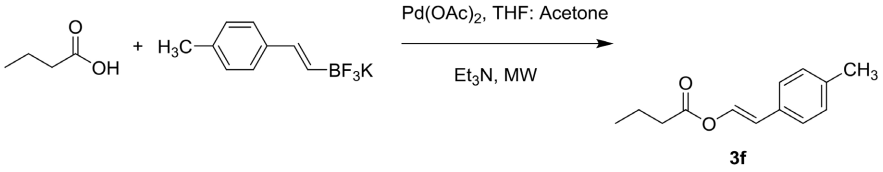

Figure 9. Synthesis of compound **3f**.

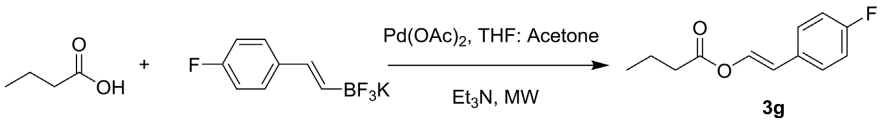

Figure 10. Synthesis of compound **3g**.

3. Conclusion

The new result of making styryl esters from Pd-inserted carboxylic acids (as expressed as RCOOPdH) and styryltrifluoroborates by cross-coupling reaction is fascinating and a new process. Styryl esters are often breakable in high temperature as well. With a small reaction scale, it is not easy to get pure compound in high amount. So, the separation process is also challenging as the final product is in very small amount in the crude reaction mixture. The importance of base in organoboron chemistry also recognized. Without base, no cross-coupling product obtained. Triethyl amine emerges as the best base in the system. We established a dual solvent system for the reaction method. The effect of phosphine ligand in palladium complex is under investigation and will report in due courses from our laboratory.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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