



Base directed palladium catalysed Heck arylation of acrolein diethyl acetal in water



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ABSTRACT

The selective Heck arylation of acrolein diethyl acetal catalysed by $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ in the presence of RAME- β -CD in water as solvent is described. Depending on the base (i.e. NaOAc or $\text{HN}(i\text{-Pr})_2$) good to high selectivity's towards, respectively, the cinnamaldehydes **2** or the 3-arylpropionic esters **1** were achieved. The results support that depending on the base different palladium intermediate complexes are formed. Using NaOAc, $\{[\text{ArPdX}(\text{H}_2\text{O})_2]\}$ complex is preferentially generated giving the cinnamaldehyde **2**. On the other hand, in the presence of $\text{HN}(i\text{-Pr})_2$, a L-type ligand, $[\text{ArPdX}(\text{HN}(i\text{-Pr})_2)(\text{H}_2\text{O})]$ or $[\text{ArPdX}(\text{HN}(i\text{-Pr})_2)(\text{HN}(i\text{-Pr})_2)]$ will be generated leading to the formation of the 3-arylpropionic ester **1**. For the last, coordinated amine participates very probably to the formation of the esters through intramolecular *syn* β -H elimination.

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1. Introduction

Cinnamaldehyde derivatives found applications in food, cosmetic agrochemical and pharmaceutical industries while 3-aryl propionic acids are common building blocks in organic synthesis. Therefore, several multi-step and costly organic methods have been reported for their synthesis [1,2]. These have been supplanted by palladium-catalysed Heck procedures [3], mainly devoted to cinnamaldehydes, from allylic alcohol [4–7] or acrolein [8–10]. In the last, some degradation was observed [11] that can be avoided by using acrolein dialkyl acetal [8]. However, the reaction was not selective and mixtures of aldehyde and ester were obtained those selectivity could be directed by the nature of the catalytic system. For example, the group of Cacchi reported a procedure in DMF at 90 °C to prepare selectively cinnamaldehydes ($\text{Pd}(\text{OAc})_2$, Bu_4NOAc , K_2CO_3 , KCl) [12] or 3-arylpropionic ester ($\text{Pd}(\text{OAc})_2$, $n\text{-Bu}_4\text{NCl}$, $n\text{-Bu}_3\text{N}$) [13]. Similarly, Santelli and Doucet reported the synthesis of cinnamaldehydes or 3-arylpropionic from 3,3-diacetoxypropene [14] or acrolein ethylene acetal [15].

In previous works, we extended this approach to a large variety of condensed aryl and heteroaryl substrates using either homogeneous [10,16] or heterogeneous [17] palladium catalysts. Under similar conditions to ours, Najera and Botella reported the preparation of cinnamaldehyde derivatives using a dimeric 4-hydroxyacetophenone oxime-derived palladacycle as catalyst [18,19]. While successful, these palladium catalysed methodologies remain linked to the use of polar organic solvents like DMF or DMAc that have been recently prohibited in most of the chemical industries.

In this context, the use of alternative non-toxic solvents appears to be very attractive. Water emerges as a good candidate in regards to previous industrial development [20] and successful transposition of Heck arylation of olefins in this media [21,22]. Initially, Beletskaya and co-workers reported the arylation of acrylic acid by diaryliodonium salts in presence of $\text{Pd}(\text{OAc})_2$ and Na_2CO_3 in water at 100 °C leading to significant yields (50–94%) of cinnamic acids [23]. The methodology was then adapted to styrene arylation [24,25] and was regarded as a green approach for the preparation of cinnamic derivatives [26]. Extension of these pioneering work concerned mainly development of water soluble systems based on hydrophilic phosphine [27] or reaction under microwave irradiations using hypervalent iodonium salts [28].

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These examples, while interesting, remain quite limited due to the exclusive use of water soluble substrates to achieve good yields. Some authors used additives in order to circumvent such limitation in which the use of phase transfer agent like tetraalkyl ammonium salts [29,30] appeared particularly successful. Originally, Jeffery reported the coupling of iodobenzene with acrylates in the presence of tetrabutyl ammonium salts [29], followed by Tsai and co-workers who used palladium cationic complexes in the presence of TBAB [30]. Recently, Iranpoor and al. reported the use of phosphazane ligands for base-free Pd(II) catalysed Heck coupling reaction of aryl iodides, bromides and chlorides in water with styrene, *n*-butylacrylate, 1-octene and cyclohexene. The palladium complex is easily separated by filtration and reused for several runs [31].

Pursuing our efforts to develop sustainable processes for fine chemical syntheses we investigated in detail the Heck arylation of acrolein diethyl acetal to cinnamaldehydes or 3-arylpropionic acids in water (Scheme 1) [32–35]. The effect of various cyclodextrins on reaction rate and selectivity was also evaluated. Indeed it is known that cyclodextrins can play a positive role in large range of water phase reaction [32–35], to the best of our knowledge no study was reported on the Heck arylation in the presence of homogeneous catalysts despite the few existing examples concerning the use of heterogeneous catalyst [36–39].

2. Experimental

They include the general information, the preparation of the catalysts, the syntheses and the analytical data (^1H NMR, ^{13}C NMR, Mass Spectra) relative to the cyclodextrins and the procedures for the catalytic tests. Mars microwave of CEM Corporation was used for the syntheses of cyclodextrin. It delivers an energy output of 800 w at a frequency of 2450 MHz. Teflon microwave-transparent XP-1500 vessels with onboard RTP-300 Plus temperature sensor control were used. With this configuration, the system regulates the microwave power out-put to maintain the desired reaction temperature.

2.1. Procedure for the synthesis of β -CD- NEt_2

β -CD-OTs (2.0 g, 1.56 mmol) in diethylamine (60 mL) was stirred and irradiated at 90 °C in closed reactor for 2 h under microwaves. After total evaporation of the amine, the crude product was dissolved in minimum distilled water and heated at 60 °C. Cooling the solution to 20 °C resulted in precipitation of white crystalline needles. Filtration on a glass filter and subsequent drying under vacuum gave β -CD- NEt_2 with 76% yield.

2.2. Procedure for the synthesis of RAME- β -CD-OTs

NaOH solution (18 g, 450 mmol, in 50 mL of water) was added dropwise to a suspension of β -CD-OTs (19 g, 15 mmol) in water (50 mL) at 0 °C over a period of 10 min. A solution of dimethylsulfate (90 mL, 950 mmol) in THF (15 mL) at 0 °C was then added dropwise to the resulting clear solution. Ethanol (10 mL) was added to the solution which was brought to room temperature and stirred for 5 h. After, THF was evaporated and the product was extracted from

the aqueous phase with chloroform (3 \times 500 mL). The organic phase was dried with anhydrous MgSO_4 . Chloroform was removed under reduced pressure to give RAME- β -CD-OTs with 57% yield.

2.3. Procedure for the synthesis of RAME- β -CD- NEt_2

RAME- β -CD-OTs (2.5 g, 1.56 mmol) in diethylamine (60 mL) was stirred and irradiated at 90 °C on closed reactor for 2 h under microwaves. After total evaporation of the amine, the crude product was dissolved in 50 mL of distilled water and the product was extracted from the aqueous phase with chloroform (3 \times 250 mL). The organic phase was dried with anhydrous MgSO_4 . Chloroform was removed under reduced pressure to give RAME- β -CD- NEt_2 with 52% yield.

2.4. Procedure for the catalytic tests

1 mmol of aryl halide, 3 mmol of acrolein diethyl acetal, 1.5 mmol base and 2 mol% of Pd-catalyst, and when applied xmol% CDs were introduced in a pressure tube. 2 mL water was added and the reactor was then placed in a pre-heated oil bath at 100 °C for 24 h under vigorous stirring. After cooling to room temperature few drops HCl 1 N were added to the reaction mixture that was extracted with 10 mL of a standard solution as EtOAc/dodecane (0.001 M). The organic layers were dried over MgSO_4 (an aliquot is removed to perform GC analyses) and evaporated under reduced pressure and the residue was then purified by flash chromatography on silica gel.

2.5. Procedure for the catalysts recycling tests

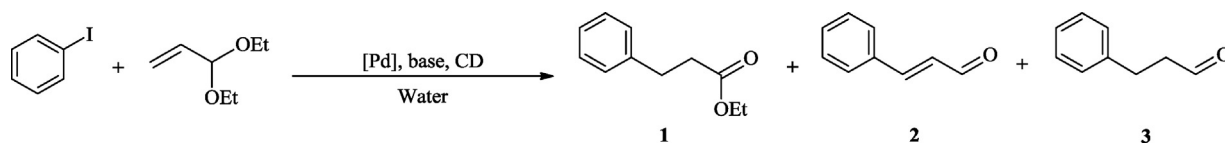
In a typical experiment fresh catalyst was used as for a standard catalytic run (2 mmol aryl halide, 6 mmol acrolein diethyl acetal, 3.5 mmol base, 2 mol% Pd-catalyst, 4 ml water, 90 °C, 24 h). After 24 hours reaction an aliquot was removed from the reaction mixture in order to perform GC-analyses and new amounts of reagents (2 mmol of aryl halide, 6 mmol of acrolein diethyl acetal, 3.5 mmol base) were added. The volume of solvent was adjusted to initial volume in order to restore the concentrations of reagents to that of the initial run. Immediately after addition, based on GC analyses, the concentration of the aryl halide was set to 100% and the concentration in products to 0%. The reaction was followed by GC for another 24 h and the procedure was repeated four times.

3. Results and discussion

3.1. Initial studies

Several commercially available palladium salts (i.e. $\text{Pd}(\text{OAc})_2$, PdCl_2 , Na_2PdCl_4 , $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$) and home-made palladium catalyst $\{\text{Pd}[\text{P}(o\text{-Tol})_3(\text{OAc})]\}_2$ (i.e. Herrmann–Beller palladacycle; prepared following reported procedure [40]) were evaluated and compared one with each other's in the Heck arylation of acrolein diethyl acetal in pure water.

In some reactions, cyclodextrins were used as additive in order to increase the catalyst activity. For this purpose, several structurally different cyclodextrins (Fig. 1) were evaluated. Except the



Scheme 1.

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