Microwave Promoted Palladium-Catalyzed Oxyarylation of Dihydronaphthalene and Chromenes by *o*-Iodophenols and its Acetates

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INTRODUCTION

Oxyarylation of olefins has been used by our group to prepare naturally occurring pterocarpans and derivatives.[1] Recently we reported the oxyarylation of dihydronaphthalene and chromenes by *o*-iodophenols under conditions favouring the cationic mechanism, reactions which were analyzed by ESI-MS.[2] In this paper we describe the scope of these oxyarylations using electron-rich **2a**-**c** and one electron-poor olefins **3** with *ortho*-iodophenols and its acetates **1a**-**h** under microwave irradiation.[3]

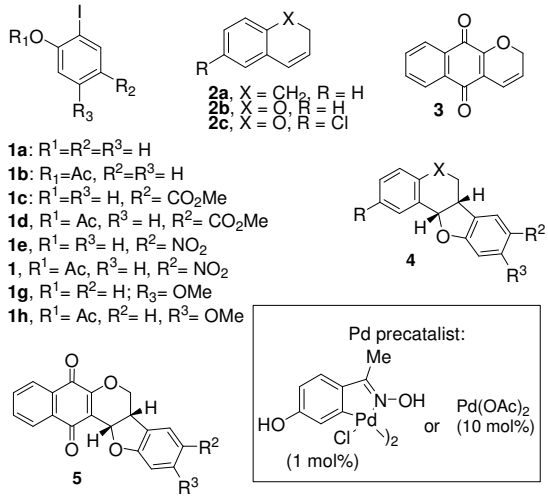
RESULTS AND DISCUSSION

In Figure 1 are shown the *ortho*-iodophenols (**1**), electron rich olefins (**2**) and one electron poor olefin (**3**) used in this work. The reaction of **1** with **2** lead to pterocarpan derivatives **4** while reaction of **1** with **3** furnish pterocarpanquinones **5**.

In one set of reactions, $Pd(OAc)_2$ (10 mol%) was used as precatalyst in the presence of Ag_2CO_3 as base, in acetone as solvent (Conditions A) while in the other set of experiments an oxime-based palladacycle (2 mol% Pd) was used as precatalyst, in the presence of Cy_2NH as base in DMA/H_2O as solvent.In both cases the reaction mixtures were submeitted to microwave irradiation, for 40 min.

The reactions studied were accelerated when accomplished under microwave irradiation (40 min. X 24 h for thermal process). Conditions A are the best choice for these reactions, for both electron-rich and electron-poor olefins, although in some cases yields obtained using the oxime-based palladacycle 5 as pre-catalyst were reasonable. The better yields of oxyarylation were observed for the reactions of electron-rich olefins with *ortho*-iodophenols substituted by electron-withdrawing groups. In contrast, for the electron-poor quinone, better yields were obtained using the electron-rich *o*-iodophenol.

Figure 1. Olefins, *ortho*-iodophenols, palladium precatalyst source and conditions for the reactions between **1** + **2** or **1** +**3** leading to **4** and **5**, respectively.



A: $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (1.5 equiv.), acetone, 60 ºC, 40 min., microwave irradiation
B: Palladacycle (2 mol% Pd), Cy_2NH (2 equiv.), DMA/H_2O, 120 ºC, 40 min., microwave irradiation

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