

Improved procedure for the α -Arylation of chromanones by *O*-Protected *ortho*-Bromophenols

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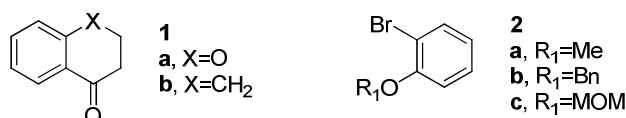
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INTRODUCTION

In recent years some procedures for the α -arylation of ketones appeared in the literature, allowing the formation of secondary, tertiary and even quaternary centers. However, only few examples on the use of *ortho*-substituted arylhalides have been described.¹ As part of a project aiming the synthesis of isoflavonoids, we report herein a study on the α -arylation of chromanone **1a** and deoxy-chromanone **1b** by *ortho*-bromophenol derivatives **2a-c**.

Figure 1. Ketones and *ortho*-bromophenol derivatives.



RESULTS AND DISCUSSION

The α -arylations studied are shown in Scheme 1, Table 1. We start our study with the reaction between **1a** by **2a** and a clean transformation of **2a** was observed under microwave irradiation, leading to **3a** (entry 1). The α -arylation goes very well even for more sterically hindered *ortho*-bromophenols **2b** and **2c** (entries 2 and 3). The same trend was observed in the reactions between **1b** and **2a-c** (entries 4-6).

We also used the oxime-derived palladacycle precatalyst **5**, synthesized by the Spanish group and previously used in several carbon-carbon bond-forming reactions in organic solvents as well as in neat water or aqueous solvents.² As shown in entry 7, a complete conversion was also observed in this case.

In contrast with the reported procedures under thermal conditions, which requires more than 2h to completion, under microwave irradiation a total conversion of *O*-protected *ortho*-bromophenols was achieved after 1h of reaction. In addition, products of α,α -diarylation, which are side products in these reactions, could not be detected in the crude

product. The chemical yield of these reactions will be reported soon.

Scheme 1. Palladium-catalyzed α -Arylation of **1** by **2**.

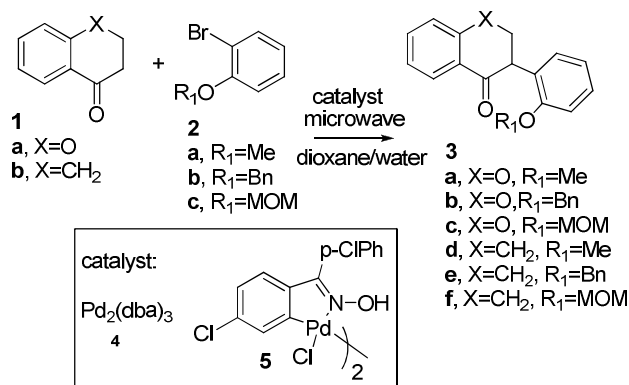


Table 1. Yields and main conditions for the reactions shown in Scheme 1.

entry	1	2	3	conversion
1	1a	a	3a	100%
2	1a	b	3b	100%
3	1a	c	3c	100%
4	1b	a	3d	100%
5	1b	b	3e	100%
6	1b	c	3f	100%
7	1b	a	3d	100%

*2.5 mol% of Pd₂(dba)₃ **4** or palladacycle **5**, 10% mol tBu₃PHBF₄, 20% mol TBAB, 1 eq. bromo-phenol **2**, 2 eq. ketone **1**, 2 eq. KOH, 120°C, 80W, 1h, Dioxane/water (4:1). Conversion measured by GC/MS. The reaction mixtures were degassed to prevent hydroxylation at the α -position in the products.

CONCLUSION

The procedure described is useful to prepare flavonoids,

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