

Palladium Catalyzed Heck Oxyarylation in Lawsone Derivatives

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INTRODUCTION

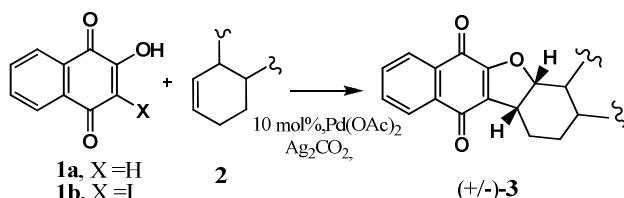
Palladium catalyzed oxyarylation of chromens, firstly reported by Horino and cols, is a powerful tool to synthesize isoflavonoids.^{1,2} Catalytic versions for this reaction were reported by Larock³ and Kiss.⁴ Mechanistic studies on the oxyarylation of olefins by *ortho*-iodophenols in the presence of silver carbonate as base, as well as the use of microwave irradiation, were recently described by our group.^{5,6} In this work we compared the Heck oxyarylation reaction of Lawsone (**1a**) and 3-iododerivative (**1b**) with olefin **2** under different conditions (Scheme 1, Table 1).

RESULTS AND DISCUSSION

We started studying the reaction between **1b** and **2**, Ag₂CO₃ as base² under refluxing acetone.^{3,4} Under thermal condition **3** was obtained in 20% yield (entry 1) but it was increased to 31% (entry 2) under microwave irradiation. However, the yield could be improved to up 57% using pinacolone as solvent, in thermal condition (entry 3). Under microwave irradiation, 50% was obtained in only 40 min. (entry 4).

Next we move our attention to the possibility of accomplishing this transformation using **1a** as substrate. In this case, a process based on C-H activation (direct insertion of Pd²⁺ on C-H bond) was expected.⁷

Scheme 1. Heck oxyarylation of **2** by **1**.



In the reaction of **1a** with **2** under thermal conditions, compound **3** could be obtained in 16% yield in acetone and could be improved to 34% in pinacolone. The study of this reaction under

microwave irradiation is due in course in our laboratory.

Table 1. Different conditions for Heck oxyarylation between **1** and **2**.

entry	1	Conditions	3 (%)
1	1b	A	20
2	1b	B	31
3	1b	C	57
4	1b	D	50
5	1a	A	16
6	1a	C	34

Condition A: 1.5 eq. Ag₂CO₃, acetone, reflux (60 °C), 18h.

Condition B: 1.5 eq. Ag₂CO₃, acetone, MW (60 °C), 40 min..

Condition C: 1.5 eq. Ag₂CO₃, pinacolone, reflux (110 °C), 18h.

Condition D: 1.5 eq. Ag₂CO₃, pinacolone, MW (110 °C), 40 min

CONCLUSION

A new oxyarylation of olefins (**2**) by 3-iodo-Lawsone (**1b**) leading to adduct **3** is described, occurring in good chemical yield, under both thermal and microwave irradiation conditions.

Another new procedure is described to preparing **3** from Lawsone **1a**, featuring a new C-H activation in this quinone. This procedure provides a greater atom economy and is under optimization.

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REFERENCES

- ¹Horino, H.; Inoue, N. *Bull. Soc. Jpn.* **1971**, *44*, 3210.
- ²Costa, P.R.R. and cols *Bioorg. Med. Chem.* **2006**, *14*, 7962 and cited references.
- ³Emrich, D. E.; Larock, R. C. *J. Organomet. Chem.* **2004**, *689*, 3756.
- ⁴Kiss, L.; Antus, S.; *Heterocycl. Commun.* **2000**, *6*, 309.
- ⁵Costa, P. R. R. *J. Organomet. Chem.* **2010**, *695*, 2062.
- ⁶Costa, P.R.R. and cols *Eur. J. Org. Chem.*, **2011** in press.
- ⁷Le Bras, J.; Muzart, J. *chem. Rev.*, **2011**, *111*, 1170.