Regioselectivity of Allenyl- and Propargyl-Phosphonate Pd-catalyzed Cross-Coupling Reactions. Reaction Mechanisms and Effect of Heteroatom Substitution.

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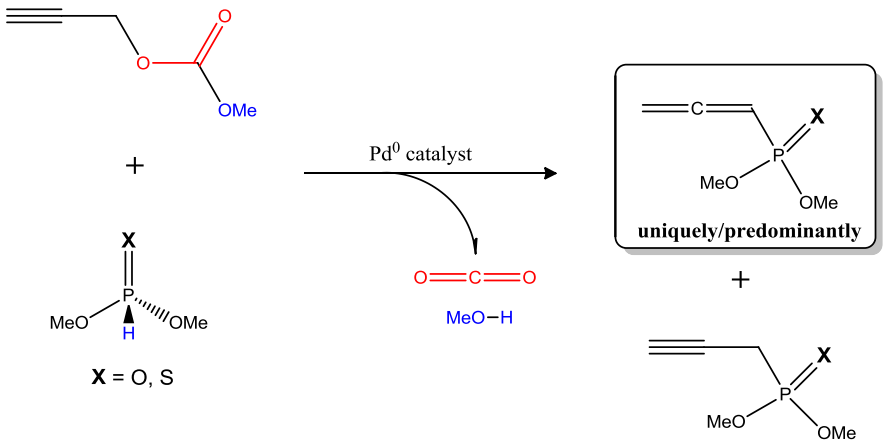
ABSTRACT

The purpose of this talk is the detailed discussion of the mechanism and sources of selectivity of a palladium-catalyzed substitution reaction between a propargylic substrate and phosphorus nucleophiles to give allenyl- (and in a mixture with propargylic-) phosphonates (Scheme 1), depending on the electronic nature of the phosphonate used.[1] The utility of this reaction is an easy accessibility to a broad spectrum of heteroatom-substituted allene-containing products present in an increasing number of natural compounds of interest in biological and pharmaceutical research. This research was done in collaboration with Prof. Fahmi Himo's group at University of Stockholm.[2]



Scheme 1. What is the reaction mechanism?

A previous seminar given by Prof. M. Solà is related with the results presented here. The conceptually interesting issue of this seminar is that, to explain the selectivity is necessary to perform an analysis of the complete free-energy surfaces since the product ratio is determined by different transition states in the respective branches of the catalytic cycle, *i.e.*, there is a defined rate-determining state of the reaction.[3]

References.

[1] JOCJH, M. Kalek, J. Stawinski, F. Himo, *Chem. Eur. J.* **2012**, *18*, 12424.
[2] See for instance: M. Kalek, T. Johansson, M. Jezowska, J. Stawinski, *Org. Lett.* **2010**, *12*, 4702; M. Kalek, J. Stawinski, *Adv. Synth. Catal.* **2011**, *353*, 1741.
[3] S. Kozuch, S. Shaik, *Acc. Chem. Res.* **2011**, *44*, 101 and references herein.