

Electroanalytical determination of the mechanism of the cobalt-catalyzed electrochemical coupling between aromatic halides and allylic acetates.

Paulo Gomes, Corinne Gosmini, Olivier Buriez,
Eric. Labbé, and Jacques Périchon

Laboratoire d'Electrochimie, Catalyse et Synthèse
Organique (LECSO), UMR CNRS 7582

2-8 rue Henri Dunant, 94320 Thiais, France.

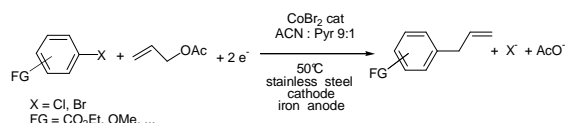
Tel : (33) 1 49 78 11 39

Fax : (33) 1 49 78 11 48

E-mail : labbe@glvt-cnrs.fr

Aromatic compounds bearing allyl substituents are of interest in the field of perfumery and biological compounds [1]. The synthetic procedures devoted to the allylation of aromatic rings generally involve organometallic reagents [2,3].

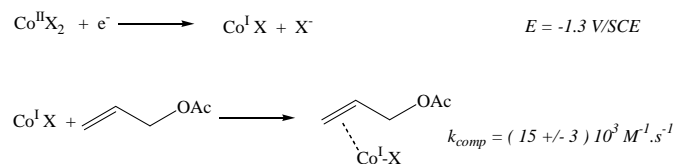
Recently, we have developed a cobalt-catalysed electrochemical coupling reaction between aromatic halides and allylic acetates [4] according to:



That process was found to allow the allylation of a variety of aromatic bromides and chlorides, functionalized by electron donating or withdrawing group in moderate to excellent yields.

Since electrochemical homocoupling of aromatic halides [5] and allyl acetates [6] also takes place with cobalt catalyst in the same medium (leading to biaryls and dienes respectively), the cobalt catalyzed allylation of aromatic halides should proceed according to a complex catalytic sequence. These observations prompted us to undertake an electrochemical study of that mechanism.

The early steps involve the electrochemical reduction of the Co^{II} precursor into Co^{I} followed by a fast complexation with the allyl acetate according to :

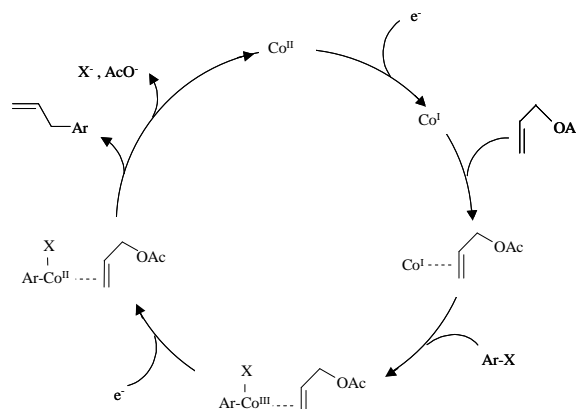


In the absence of aromatic halide, the $(\eta^2\text{-allyl})\text{cobalt}(\text{I})$ complex slowly undergoes an intramolecular oxidative addition leading to $(\eta^3\text{-allyl})\text{cobalt}(\text{III})$. This latter species is reduced at the same potential as the original Co^{II} catalyst precursor, to give $(\eta^3\text{-allyl})\text{cobalt}(\text{II})$ which reacts on another allyl acetate molecule to release the corresponding diene.

We have established that the aromatic halide Ar-X undergoes an oxidative addition on the $(\eta^2\text{-allyl})\text{cobalt}(\text{I})$ complex to give a $(\eta^2\text{-allyl})\text{aryl}(\text{III})\text{cobalt}(\text{III})$ species. We have determined the rate constants for the oxidative addition for several aromatic halides and for different allylOAc / Co ratios. It comes out that the rate constants

strongly depend on the nature of both the halide and the substituent on the aromatic ring. As a matter of fact, the rate constants are following the expected Hammet plot for oxidative addition reaction.

The coordinating effect of the allyl acetate is confirmed, since an increase of its concentration results in a lower rate constant. That latter $(\eta^2\text{-allyl})\text{aryl}(\text{III})\text{cobalt}(\text{III})$ species is reduced at the same potential as the original $\text{Co}^{\text{II}} / \text{Co}^{\text{I}}$ couple, leading to $(\eta^2\text{-allyl})\text{aryl}(\text{II})\text{cobalt}(\text{II})$. The arylallyl compound is most likely obtained through an intramolecular $\text{S}_{\text{N}}2$ reaction. The overall mechanism may therefore be depicted in Scheme 1 :



Scheme 1
Overall mechanism proposed for the cobalt catalyzed allylation of aromatic halides.

References:

- [1] E. Wenkert, J.B. Fernandes, E.L. Michelotti, C.S. Swindell, *Synthesis* **1983**, 701-703.
- [2] M.S. Karasch, O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Coustable Ed., London, 1954.
- [3] a) L. Zhu, R.M. Wehmeyer, R.D. Rieke, *J. Org. Chem.* 1991, *56*, 1445-1453.
b) F. Dübner, P. Knochel, *Angew. Chem. Int. Ed. Engl.* 1999, *38*, 379-381.
- [4] P. Gomes, C. Gosmini, J. Périchon, *J. Org. Chem.* Accepted.
- [5] a) O. Buriez, C. Cannes, J.Y. Nédélec, J. Périchon, *J. Electroanal. Chem.* 2000, *495*, 57-61.
b) O. Buriez, J.Y. Nédélec, J. Périchon, *J. Electroanal. Chem.* 2001, *506*, 162-169.
- [6] O. Buriez, E. Labbé, J. Périchon, *J. Electroanal. Chem.* submitted.

