

44th



International Conference on
Coordination Chemistry



Rimini 202  **2022**

ABSTRACT BOOK

**August 28th - September 2nd
2022**

Rimini - Italy

www.iccc2022.com



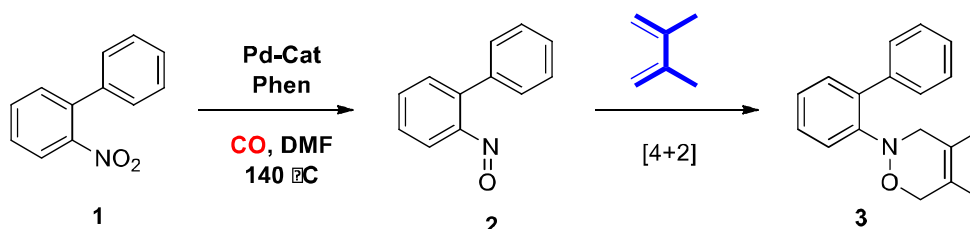
THE MYSTERY BEHIND THE REDUCTIVE CYCLIZATION REACTION OF O-NITROBIPHENYLS: A MECHANISTIC STUDY

Manar Ahmed FOUAD,^{1,2} Doaa R. RAMADAN,^{1,2} Francesco FERRETTI,¹ Fabio RAGAINI¹

¹ Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy
E-mail: manar.abdellatif@unimi.it

² Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt

The use of nitroarenes to synthesize various *N*-heterocycles through metal catalyzed reductive cyclization reactions has attracted much interest. Unfortunately, the mechanism behind these kinds of reactions is poorly studied due to the instability of the intermediates formed during the reaction, both organic intermediates and metal complexes.^[1] Here we report our experimental studies on the mechanism of the catalytic reductive cyclization reaction of *o*-nitrobiphenyls to carbazoles. Nitroso compounds, are usually considered as intermediates along the reduction of nitro compounds by CO.^[2,3] However, under catalytic conditions, nitroso compounds are not generally observed. This is due to the fact that nitrosoarenes are more easily reduced than their corresponding nitroarenes so that they react faster than the starting compounds and do not accumulate during the catalytic cycle. Hence all the previous attempts to obtain nitrosoarene met with failure.^[3,4] Differently from other nitroso compounds, *o*-nitrosobiphenyl **2**, intermediate in the formation of carbazole from *o*-nitrobiphenyl **1**, is a relatively stable compound which we were able to intercept during the reductive cyclization of **1**. **2** was trapped by addition of a conjugated diene to the reaction mixture allowed to trap **2** through the formation of the oxazine **3** (Scheme 1). A kinetic study of the thermal cyclization of *o*-nitrosobiphenyl in DMF at 100 °C was also performed to elucidate the role of Pd catalyst, bases and other additives on the cyclization step that follows the first reduction of the nitro group. On the base of previous theoretical studies^[5] proposing that 1,5-hydrogen migration is involved in the 1,5-electrocyclization of nitrosobiphenyl, and our new experimental data, we thus shed some light on the role of the different components of the catalytic system on the reaction mechanism behind the reductive cyclization reaction.



Scheme 1. Trapping of *o*-nitrosobiphenyl intermediate.

References:

- [1] Ferretti, F.; Ramadan, D.R.; Ragaini, F. *ChemCatChem*, **2019**, *11*, 4450.
- [2] Ferretti, F.; Formenti, D.; Ragaini, F. *Rendiconti Lincei*, **2017**, *28*, 97.
- [3] Fouad, M.A.; Ferretti, F.; Formenti, D.; Milani, F.; Ragaini, F. *Eur. J. Org. Chem.* **2021**, 4876.
- [4] Davies, I.W.; Smitrovich, J.H.; Sidler, R.; Qu, C.; Gresham, V.; Bazaral, C. *Tetrahedron*, **2005**, *61*, 6425.
- [5] Davies, I.W.; Guner, V.A.; Houk, K.N. *Org.Lett.*, **2004**, *6*, 743.