

XXVII CONGRESSO NAZIONALE DELLA SOCIETÀ CHIMICA ITALIANA

LA CHIMICA GUIDA LO SVILUPPO SOSTENIBILE

14-23 SETTEMBRE 2021



Heterocycles from nitro compounds: CO surrogates in the Pd-catalyzed synthesis of carbazoles

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Palladium complexes with phenanthroline ligands are so far the most effective catalysts for the reductive cyclization of nitroarenes by carbon monoxide to yield a variety of N-heterocyclic compounds.¹ Despite the high efficiency of many of these reactions, they have not become of widespread use. This is mainly attributed to the need for pressurized CO (requiring specific safety measures). In the aim of turning this kind of reaction into a "general tool" for the synthetic chemist, we developed a procedure based on the use of formates as an *in situ* source of CO. The reaction can be performed in a glass pressure tube, a cheap equipment accessible to every laboratory. The method was employed for the synthesis of indoles² and oxazines,³ affording the products in very good to excellent yields. However, when applied to the cyclization of o-nitrobiphenyls to carbazoles the method gave only poor yields. Herein we report a modified catalytic protocol for carbazole synthesis that tolerates both air and moisture and can be performed using undried and undistilled commercial DMF. The catalytic method has wide applicability and can be easily scaled up to gram scale reaction. Studies on the role of the metal in the cyclization step will be also discussed.

Scheme 1. Reductive cyclization of 2-nitrobiphenyls to carbazoles using formates as CO source.

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