Book of Abstracts

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OC25 CO From Our Worst Enemy to Our Best Friend: Pd-Catalyzed Reductive Cyclization of β-Nitrostyrenes Using Phenyl Formate as a CO Surrogate

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The reduction of suitably substituted organic nitro compounds by CO, catalyzed by palladium-complexes, is a valuable method for the preparation of a variety of *N*-heterocyclic compounds.[1] Despite the high efficiency of many of these reactions, the use of pressurized CO is a drawback since it requires the use of high-pressure equipment and CO lines and the presence of the corresponding safety measures. This limits the application of this kind of reactions as practical synthetic methods. 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 phenyl formate as an efficient *in-situ* CO surrogate. Recently, our group employed phenyl formate in the palladium-catalyzed reductive cyclization of 2-nitrostyrenes to afford indoles [2] and in the reduction of nitroarenes in the presence of conjugated dienes to give oxazines.[3] It was found that phenyl formate is the most effective CO source and the desired products were obtained with selectivities and yields that in most cases are higher than those previously reported using pressurized CO. The reaction can be performed in a glass pressure tube, a cheap equipment accessible to every laboratory. Here, we report our results regarding the use of phenyl formate as a CO surrogate in the synthesis of indoles by reductive cyclization of β-nitrostyrenes, catalyzed by $PdCl_2(MeCN)_2$ + 1,10-phenanthroline. It has been found that satisfactory results are obtained when the starting nitrostyrene has an aryl substituent at the *alpha* position. On the other hand, in the absence of such substituents, only moderate yields of indole have been achieved since the base required to degrade the formate can also catalyze the oligo-polymerization of the starting styrene.[4]

Figure 1: Schematic Representation of Synthesis of indoles from β-nitrostyrenes using HCOOPh as a CO surrogate.

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[4] F. Ferretti, M. A. Fouad, F. Ragaini, *Catalysts* **2022**, *12*, 106.