XI PHD DAY BARI

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28 Marzo 2014

9:00/13:00 – 15:00/18:40

Synthesis of nitrogen heterocycles by intramolecular cyclization of nitro-olefins attached to five-membered heterocycles, catalyzed by palladium complexes and with carbon monoxide as the reductant.

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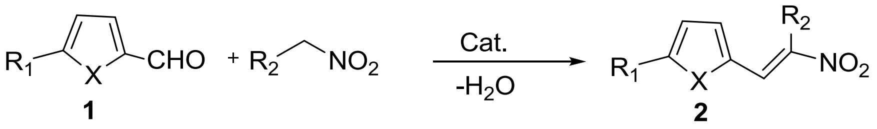
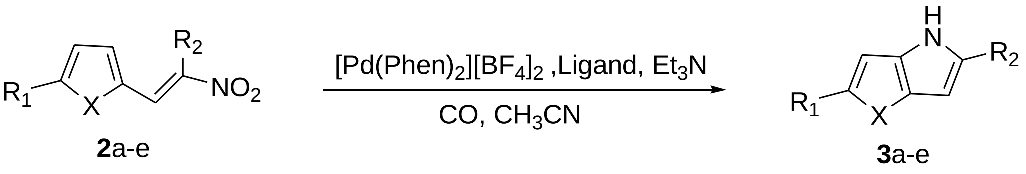
Abstract

Research in our unit recently showed that reducive cyclization of β-nitrostyrenes catalyzed by palladium/phenanthroline complexes and with CO as a reductant affords indoles in good yields.[1] The reaction proceeds by the activation of an aryl C-H bond. We decided to extend such cyclization reaction to other heterocyclic systems, although it is known that the activation of a C-H bond of electron-rich five member heterocycles is a more difficult reaction. Nitro olefins attached to 5-membered heterocyclic compounds **2a-e** were prepared by the Henry reaction and fully characterized by ^{1}H-NMR, ^{13}C-NMR and elemental and mass analyses. Subsequent reductive cyclization catalysed by palladium-phenanthroline complexes under CO pressure afforded A10 π aromatic compounds, isoelectronic with pentalenyl dianion, and containing a pyrrole ring fused to another 5-membered heterocyclic compound (**3a-e**). Compound **2c** was chosen as a model compound for the optimization of the experimental conditions. Among many tested ligands 4,7-dimethoxyphenanthroline showed good results for both conversion and selectivity. The optimization of temperature, CO pressure, nature of the base, type of ligand, reaction time and solvent are in progress.





a, X = O, $R_1 = CH_3$, $R_2 = CH_3$
b, X = S, R_1 = H, $R_2 = CH_3$
c, X = NCH_3, R = H, $R_2 = CH_3$
d, X = NAc, R= H, $R_2 = CH_3$
e, X = S, R_1 = H, R_2 = COOEt

References

1 F. Ferretti, S. Muto, M. Hagar, E. Gallo, F. Ragaini, manuscript in preparation..

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