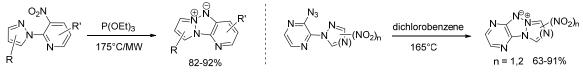
NITRENE-BASED N-N BOND FORMATION: AN EFFICIENT METHOD TOWARDS NITROGEN-RICH TRICYCLIC TRIAZAPENTALENES

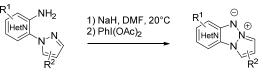
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Triazapentalenes are fascinating compounds, owing to their original structure and their applications. As a matter of fact, these heterocycles containing a 1,2,3-triazolium ylide core can exhibit fluorescent and energetic properties. The synthesis of tricyclic or tetracyclic derivatives are rare and rely exclusively on intramolecular N-N bond formation through electrophilic nitrene intermediates. In our first efforts, we described the synthesis of new nitrogen-rich tricyclic triazapentalene derivatives, by using the nitro [1] or the azido [2] group as nitrene precursors, under thermolysis conditions.



More recently, we designed a new access to nitrenes starting from heteroaromatic amines (NH₂), using a hypervalent iodine reagent. This promoted the formation of the desired zwitterionic N-N bond under catalyst-free and mild conditions, thus extending the scope to diversely functionalized triazapentalene structures, including previously unknown heterocyclic systems [3].



HetN = pyridine, pyrazine, pyrimidine, pyridazine

^[1] C. Nyffenegger, E. Pasquinet, F. Suzenet, D. Poullain, C. Jarry, J.-M. Léger, G. Guillaumet, *Tetrahedron* 2008, 64, 9567.

^[2] C. Nyffenegger, E. Pasquinet, F. Suzenet, D. Poullain, G. Guillaumet, Synlett, 2009, 1318.

^[3] M. Daniel, M.-A Hiebel, G. Guillaumet, E. Pasquinet, F. Suzenet, manuscript in preparation.