

DEAROMATIZATION OF ELECTRON POOR ARENES BY (4+2) CYCLOADDITION REACTION

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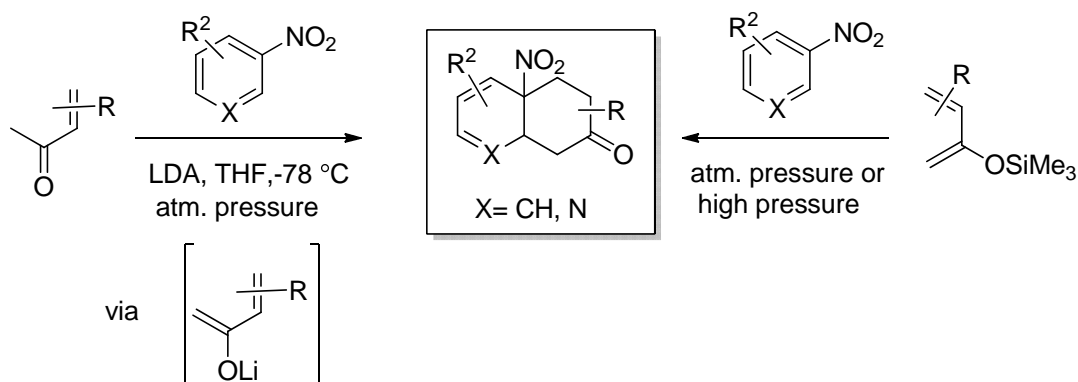
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Aromatic compounds are common substrates, obtained whether from the petrochemical industry or from natural products. Thus, important efforts have been made to convert these simple and easily available molecules into complex 3D structures of synthetic interest such as polycycles featuring tetrasubstituted centers, for example, useful in the synthesis of natural or pharmaceutical products ^[1]. Even if several efficient dearomatizing methods have been reported on phenol ^[2] and indole derivatives ^[1,3] for instance, the development of complementary methodologies is still needed.

In this context, (4+2) cycloadditions represent an attractive approach to obtain complex polycyclic compounds from simple aromatic substrates. In the course of this work, we have examined the reactivity of different nitroaromatics towards silyloxydienes in Normal Electron Demand Diels-Alder cycloadditions (Scheme 1, right).

A complementary nucleophilic activation of the diene, through the formation of its lithium dienolate derivative has also been studied to dearomatize these derivatives (Scheme 1, left). Results regarding the efficiency and selectivities of these novel cycloadditions and annulations will be presented.



Scheme 1

[1] See for instance a) S. P. Roche et al., *Angew. Chem. Int. Ed.*, 2011, 50, 4068-4093. b) S. L. You, et al., *Angew. Chem. Int. Ed.* 2012, 51, 12662-12686. c) R. Fan et al., *Org. Biomol. Chem.*, 2014, 12, 4807-4815.

[2] S. Quideau et al., *Angew. Chem.*, 2014, 53, 9860-986.

[3] G. Vincent et al., *Tetrahedron Lett.*, 2015, 56, 4413-4429.