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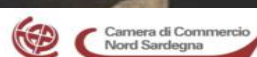
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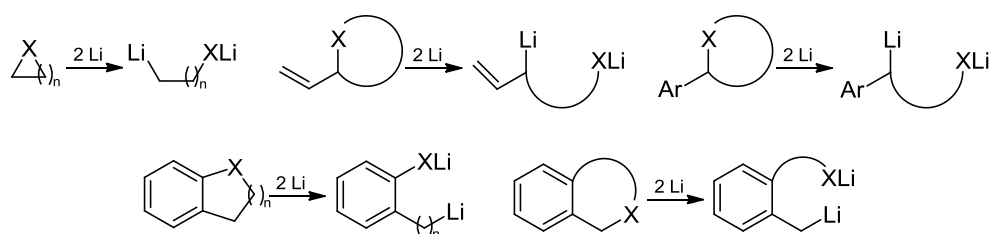
Green and Convenient Arene-Catalyzed Reductive Lithiation of Heterocyclic Compounds

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In the last decades reductive lithiation established itself as a particularly powerful procedure for the generation of functionalized organometals. In addition, the enormous role of this reaction in the reductive ring opening and functionalization of heterocycles has been reported (Scheme 1) [1].



Scheme 1. Reductive lithiation of different classes of heterocyclic compounds; X = NR, O, S; n = 1,2.

Almost always, the efficiency of this reaction strongly depends on the presence of a polycyclic aromatic hydrocarbon (PAH), employed as an electron shuttle, either in catalytic (CA) or stoichiometric (SA) amounts. Indeed, formation of their soluble and intensively coloured radical anions is considered to speed up the electron-transfer process, thus avoiding formation of by-products [2]. According to its ability to dissolve PAH's radical anions, tetrahydrofuran (THF) emerged as the solvent of choice for these reactions [3]. However, several factors (water solubility, relatively low boiling point, expensive purification, drying and recycling) makes THF a poorly eco-efficient solvent. Herein we report on the employment of 2-methyltetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME) as alternative green solvents for the generation of PAH's radical anions and their employment in the generation of organolithium reagents.

Accordingly, critical experiments were performed for the generation of lithium radical anions of several PAHs and a diene in both solvents, under both CA and SA protocols. Almost all of the above mentioned hydrocarbons rapidly generate radical anions with different fascinating visible colors at 0 °C. Based on this, influence of different electron shuttles and their efficiency in the reductive lithiation of *N*-phenylaziridine, phthalan will be disclosed. Moreover, we will report an interesting example of chemoselectivity concerning to the reductive lithiation of 4-chlorobenzyl methyl ether in a green solvent.

References:

- [1] Yus, M.; Foubelo, F. *Adv. Heterocycl. Chem.*, **2006**, 91, 135-158, and references therein.
- [2] Azzena, U., Pilo, L., Piras, E. *Tetrahedron*, **2000**, 56, 3775-3780, and references therein.
- [3] Cohen, T., Kreethadumrongdat, T., Liu, X.; Kulkarni, V. *J. Am. Chem. Soc.*, **2001**, 123, 3478-3483.