

RADICALS AND CATIONS. RECENT DEVELOPMENTS

For several years now, our team has been developing two main research axes, one focused on the development of new radical processes and the other one on the use of silicon reagents in organic synthesis. During this talk will be presented some recent examples illustrating our progress in these two areas.

The first part of the presentation will thus focus on the development of free-radical additions to olefins. The recent advent of photoredox catalysis has led us to consider new activation pathways, in the field of radical additions of sulfonyl reagents to olefins, in the context of the total synthesis of Leucophyllidine, a terpene indole alkaloid. Light activation also provides solutions for medicinal chemistry and synthesis of polymers. Our efforts on the development of new methods to access isocyanates, urethanes and polyurethanes will be discussed, including scope and limitations of the methodology along with mechanistic aspects.

In a second part, our ongoing studies on the stereochemistry of chiral silyl cations will be presented. In contrast to carbocations, which existence was recognized and firmly established in 1901, silylium ions (R_3Si^+) have remained for a long time elusive species and it is only in 2002 that the molecular structure of a truly trivalent cationic silicon species was determined through X-ray diffraction studies. Silylium ions are exceptionally electrophilic, which may also prevent their use in catalysis. Intramolecular interaction between a Lewis basic site and the silicon center has however been shown to pacify the silylium, offering new opportunities for the development of these unusual Lewis acids. Our laboratory has recently developed chiral silyl cations with axial and Si-centered chirality, which preparation and characterization will be shown. The configurational stability of these cations, the chiral memory or the complete axial-to-central chirality transfer, supported by computational studies, will be discussed.

Some recent publications

1. A. Jatoi Hussain, G. G. Pawar, F. Robert, Y. Landais, *ChemComm.* **2019**, 55, 466-469
2. G. G. Pawar, F. Robert, E. Grau, H. Cramail, Y. Landais, *ChemComm* **2018**, 54, 9337-9340
3. V. Pirenne, G. Kurtay, S. Voci, L. Bouffier, N. Sojic, F. Robert, D.M. Bassani, Y. Landais, *Org. Lett.* **2018**, 20, 4521-4525
4. H. Hassan, V. Pirenne, M. Wissing, C. Khair, A. Hussain, F. Robert, Y. Landais, *Chem. Eur. J.* **2017**, 23, 4651-4658
5. R. Beniazza, V. Liautard, C. Poittevin, B. Ovidia, S. Mohammed, F. Robert, Y. Landais, *Chem. Eur. J.* **2017**, 23, 2439-2447
6. H. Hassan, S. Mohammed, F. Robert, Y. Landais, *Org. Lett.* **2015**, 17, 4518-4521
7. P. Ducos, V. Liautard, F. Robert, Y. Landais, *Chem. Eur. J.* **2015**, 21, 11573-11578.