

Seminar

A Journey from Radical Azidation Reaction to Metalloradical Catalysis via Cascade: Mechanistic Study and Application

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Radical chemistry was radically neglected in comparison to ionic chemistry until the seminal discovery of the “triphenylmethyl radical” by Gomberg. Despite rapid growth of synthetic radical chemistry, the application of it in the strategic planning of preparative organic synthesis remained highly limited.^[1] Specially, taming organic radicals to the required extent is still a challenging task during the design of new stereoselective radical reactions.^[2] In this regard, metalloradical chemistry is going to play a vital role to control the stereoselectivity of radical reactions.

First part of the lecture will be focused on the development of a concise strategy to streamline the synthesis of azabicyclic ring systems in a stereoselective fashion involving radical azidation, Intramolecular Schmidt Reaction and nucleophilic additions of carbanions.^[3-5] In the second part, development of a copper catalyzed biomimetic C-H bond oxidation under aerobic conditions and a detailed mechanistic study will be presented.^[6] The remaining time of the talk will be focused on the development of a nickel centred metalloradical induced 1,3-H atom transfer reaction to install E-olefins from the terminal position to internal position with >99:1 E/Z selectivity.^[7]

References:

1. Radicals in Organic Synthesis, Vol. 2 (Eds.: Renaud, P.; Sibi, M. P.), Wiley-VCH, Weinheim, 2001. Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group II, Vol. 13 (Ed.: H. Fischer), Springer, Berlin, 1983.
2. Curran, D. P.; Porter, N. A.; Giese, B. Stereochemistry of Radical Reactions: Concepts, Guidelines, and Synthetic Applications; Wiley-VCH: Weinheim, Germany, 1996; p 281
3. Kapat, A.; Nyfeler, E.; Giuffredi, G. T.; Renaud, P., J. Am. Chem. Soc. 2009, 131, 17746-17747.
4. Kapat, A.; König, A.; Montermini, F.; Renaud, P., J. Am. Chem. Soc. 2011, 133, 13890-13893.
5. Lapointe, G.; Kapat, A.; Weidner, K.; Renaud, P., Pure and Applied Chemistry 2012, 84, 1-9.
6. Tsang, A. S#. K.; Kapat, A.#; Schoenebeck, F., J. Am. Chem. Soc. 2016, 138, 518-526. (#T.A-S and AK contributed equally)
7. Kapat, A.; Sperger, T.; Guven, S.; Schoenebeck, F., Science, 2019, 363, 391-396.

Monday, Mar 23rd 2020

4:00 PM (Tea/Coffee at 3:30 PM)

Seminar Hall, TIFR-H