

Ph.D. Seminar II

Stereo and Regioselective Nitroso Aldol Reactions using Nitrosocarbonyl Intermediates

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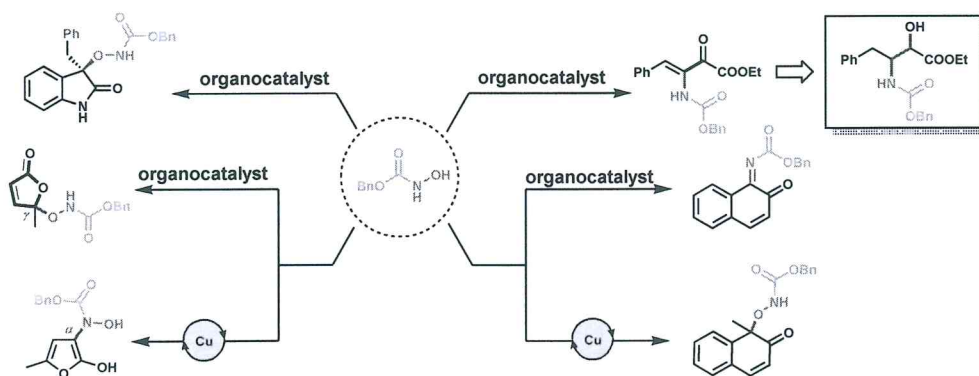
Guide: Dr. Md. Mahiuddin Baidya

Date: 29.10.19

Time: 3.00 pm, Venue: 310

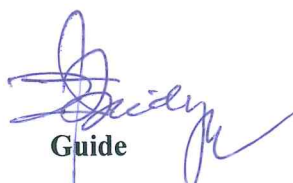
Abstract

Synthetic planning harnessing ambident nature of reaction partners is highly alluring as dissimilar bonds can be fabricated from a single source through judicious tuning of the reaction conditions.^{1,2} In this context, nitrosocarbonyl intermediates have attracted considerable attention.² They are prototypes of ambident electrophile and have extensively been utilized in diverse C–N and C–O bond forming processes through aldol, ene, Henry, and various types of cycloaddition reactions.³ In this context, we were interested in developing step-economic nitroso aldol reaction under mild conditions for the production of heteroatom functionalized small molecules in regio and stereoselective fashion. We have developed a practical and flexible strategy towards α -hydroxy- β -amino carbonyls, an important biological motif, based on an organocatalytic cross aldol reaction of in situ generated nitrosocarbonyl intermediates followed by hydrogenation.⁴ Further advancement in nitroso chemistry is showcased by the divergent reactivity of fleeting nitrosocarbonyls in catalytic oxidative dearomatization of β -naphthols,⁵ where both the oxyamination and aminoxylation products were accomplished selectively. The usefulness of nitroso aldol reaction has also been shown in catalyst controlled regioselective nitrosocarbonyl aldol reaction of angelicalactones. Further we have developed a mild method for the construction of enantioenriched 3,3-disubstituted oxindoles through a stereoablative aminohydroxylation of 3-halo oxindoles with *N*-hydroxycarbamates using a cinchona alkaloid derivative catalyst. In this seminar, details of these developments will be presented.



Scheme 1. Stereo- and Regioselective Nitroso Aldol Reactions using Nitrosocarbonyl Intermediates

References: (1) (a) *Ambident Anions*; Beletskaya, I. A.; Kurts, A. L.; Reutov, O. A., Ed.; Springer, 1983. For a review on ambident reactivity: (b) Mayr, H.; Breugst, M.; Ofial, A. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 6470. (2) (a) Palmer, L. I.; Frazier, C. P.; Read De Alaniz, J. *Synthesis* **2014**, *46*, 269. (b) Memeo, M. G.; Quadrelli, P.; *Chem. Rev.* **2017**, *117*, 2108. (c) Dana, S.; Ramakrishna, I.; Baidya, M. *Synthesis* **2017**, *49*, 3281. (3) (a) Maji, B.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 753. (b) Adam, W.; Krebs, O. *Chem. Rev.* **2003**, *103*, 4131. (c) Reddy, M. K.; Mallik, S.; Ramakrishna, I.; Baidya, M. *Org. Lett.* **2017**, *19*, 1694. (d) Bodnar, B. S.; Miller, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 5630. (4) Mallik, S.; Bhajammanavar, V.; Ramakrishna, I.; Baidya, M. *Org. Lett.* **2017**, *19*, 3843. (5) Mallik, S.; Bhajammanavar, V.; Mukherjee, A. P.; Baidya, M. *Org. Lett.* **2019**, *21*, 2352.


Guide


28.10.19
Seminar Coordinator


Head of the Department

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