XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Brønsted Acid Catalyzed O- to N-Alkyl Migratory Rearrangement in Pyridine

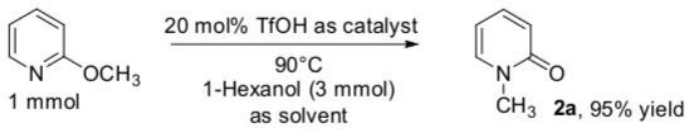
Nelson H. Morgon[a], Aguinaldo R. de Souza[b], Abhishek K. Mishra[c], Srijit Biswas[c]

[a]*Universidade Estadual de Campinas, Instituto de Química, Campinas, SP, Brazil*

[b]*Universidade Estadual Paulista, Departamento de Química, Bauru, SP, Brazil*

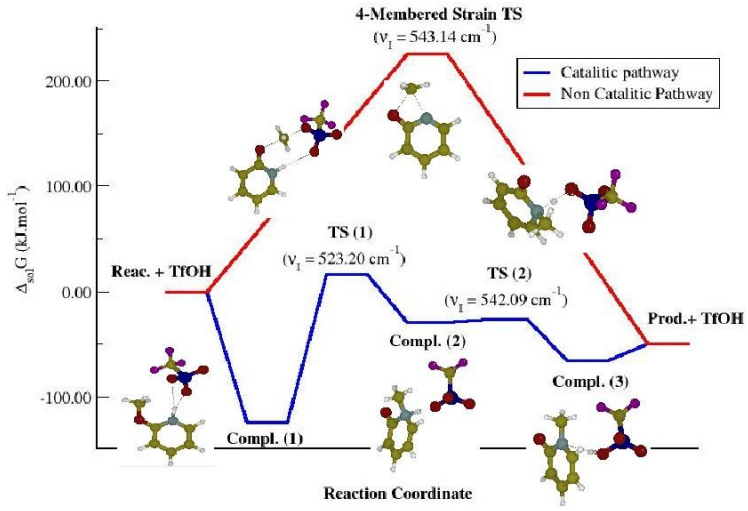
[c]*Centre of Biomedical Research (CBMR), SGPGIMS Campus, Raebareli Rd, Lucknow 226014, Uttar Pradesh,India*

Abstract: The reaction Brønsted acid catalyzed O- to N-alkyl migratory rearrangement in pyridine (Fig. 1) is consistent to the research interest to develop metal and ligand free methods to reduce environmental impact and increase atom efficiency. In this reaction also the generated substituted pyridones are a very important core structures found in various bio-active natural products. It is know Brønsted acid having O=X-OH moiety can act as bifunctional catalyst and can simultaneously activate two reactive centres in a unique way via a cyclic transition state[1].



TfOH = Trifluoromethanesulphonic acid

Electronic and molecular structures of compounds originated from the reaction Brønsted acid catalyzed O- to N-alkyl migratory rearrangement in pyridine were theoretically investigated through theorectical calculation. These calculations were performed using DFT employing the hybrid exchange-correlation functional B3LYP. Geometry optimizations and evaluation of harmonic frequencies were performed at the B3LYP/6-311++G(2d,p). The optimized structures were confirmed to be minima by vibrational frequency analysis. The single point energy calculations were carried out at B3LYP/6-311++G(3df,2p) level on corresponding optimized geometries. Solvent effects are included using the SMD Solvation Model. All computations were performed using the Gaussian 09, Revision D.01 package[2]. The non-catalytic is an unfavourable pathway. The reaction may be proceeding thorough the following mechanism involving two transition states - TS (1) and TS(2) (Fig. 2).



The full mechanism diplayed at Fig.2 is:

2-Methoxypyridine (Reactant) + TfOH → Hydrogen transfer → Complex (1) → TS (1) → Complex (2) → TS (2) → Complex (3) → 1-Methyl-2-pyridone (Product) + TfOH

Key-words: 2-Methoxypyridine, 1-Methyl-2-pyridone, B3LYP, SMD

Support: The authors gratefully acknowledge financial supports from FAPESP and CNPq (Brazilian Science Funding Agencies) as well as the computational facilities of GridUNESP. SB also acknowledge the financial supposts from DST (INSPIRE Faculty Award) for the experimental works.

References:

[1] A. K. Mishra, S. Biswas, J. of Org. Chem. 81(6), 2355 (2016).
[2] http://www.gaussian.com