

Balticum Organicum Syntheticum

3-6 July 2016 Riga, Latvia

PROGRAM AND ABSTRACTS

NUCLEOPHILIC RING OPENING OF PROTECTED AND UNPROTECTED SMALL N-HETEROCYCLES IN LIQUID SO₂

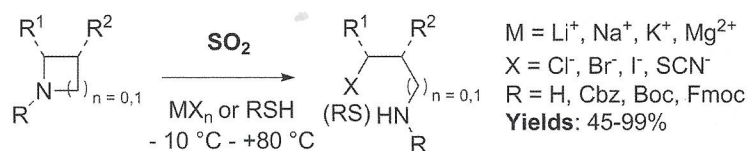
Jevgeņija Lugiņina, Māris Turks

Faculty of Materials Science and Applied Chemistry, Riga Technical University,

P. Valdena 3/7, Riga, LV-1048, Latvia

maris_turks@ktf.rtu.lv

In the field of organic chemistry SO₂ is used as a solvent, catalyst and a reagent.¹ It has a broad liquid range (from -75°C to -10°C) and due to the high dipole moment (1.6 D) it has high solvation power for ionic and covalent compounds. By dissolving inorganic and organic substances in liquid SO₂ it is possible to perform S_N2 type reactions, including nucleophilic ring opening of small N-heterocycles under mild reactions conditions described by us.²



Here we present a new synthetic process of nucleophilic ring opening reactions (NRORs) of different protected and unprotected aziridines and azetidines with I and II group metal halides and S-nucleophiles in liquid sulfur dioxide. The reactions were carried out in three temperature modes and the efficiency of each N-heterocycle ring opening reaction was monitored in several solvents in parallel experiments: SO₂(liq.), DMSO, MeCN, TFE and acetone. Results showed that that NRORs of N-heterocycles in liquid SO₂ proceeds noticeably faster and cleaner than in classical solvents. For example, reaction of Cbz-protected aziridine and NaCl takes only 12 h at room temperature in liquid SO₂ to form expected halo-carbamate in almost quantitative yield while similar reaction in classical solvents did not proceed at all.

References

1. a) Lugiņina, J. *Synlett* **2014**, 25, 2962. B) Deeming, A. S.; Emmett, E. J.; Richards-Taylor, C. S.; Willis, M. C. *Synthesis* **2014**, 46, 2701.
2. Lugiņina, J.; Uzuleņa, J.; Posevins, D.; Turks, M. *Eur. J. Org. Chem.* **2016**, 1760.