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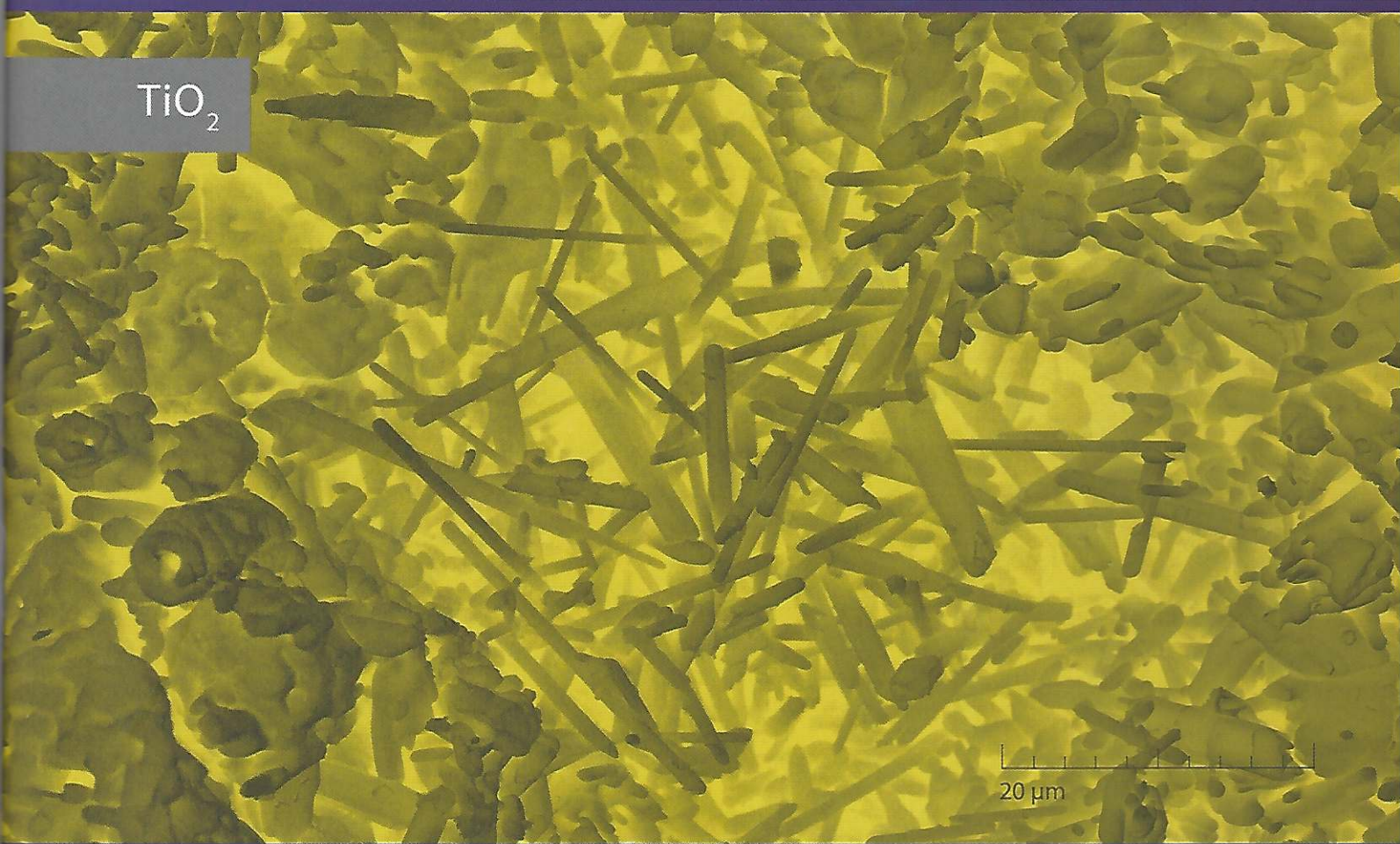
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# Material Science and Applied Chemistry

Materiālzinātne  
un lietišķā ķīmija

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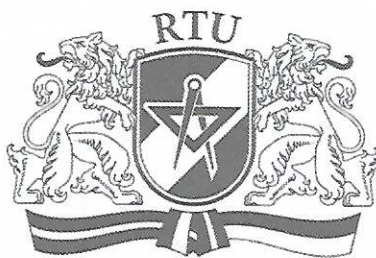
TiO<sub>2</sub>



Electron microscopy image

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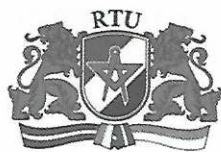
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# Sulfur Dioxide – Powerful Solvent for Nucleophilic Ring Opening Reactions of Small *N*-Heterocycles

Jevgeņija Lugiņina,

Faculty of Material Science and Applied Chemistry, Riga Technical University, P. Valdena 3, Riga, LV-1007, Latvia  
E-mail: maris\_turks@ktf.rtu.lv

## INTRODUCTION

For a long term sulfur dioxide has proven itself as an important compound to a range of different industries. It has been used as a bleaching agent, food additive and disinfection agent in food and particularly in wine making for at least 3000 years. Up to this day it is used as a wine additive in concentrations of 20 ppm – 40 ppm. In organic chemistry SO<sub>2</sub> has shown a great potential as a solvent, reagent and catalyst [1]. Surprisingly, despite all these facts sulfur dioxide has not entered the “classic toolbox” of synthetic organic chemist as an everyday-solvent. Hence, we investigate the use of sulfur dioxide as a solvent for organic transformations.

The aziridine and azetidine functionalities represent valuable small ring *N*-heterocycles in modern synthetic chemistry, because of their versatility as significant building blocks for chemical bond elaborations and functional group transformations [2]. Modifications of these aza-heterocycles can lead to the formation of various classes of compounds, such as heterocycles [3], alkaloids [4] and non-natural amino acids [5]. The reactivity of aziridines and azetidines strongly depends on variations of ring substituents, activation of nitrogen atom and ring strain. Due to the latter, common transformations of these heterocycles are the nucleophilic ring-opening reactions (NRORs). NRORs have been exhaustively described in excellent reviews [6].

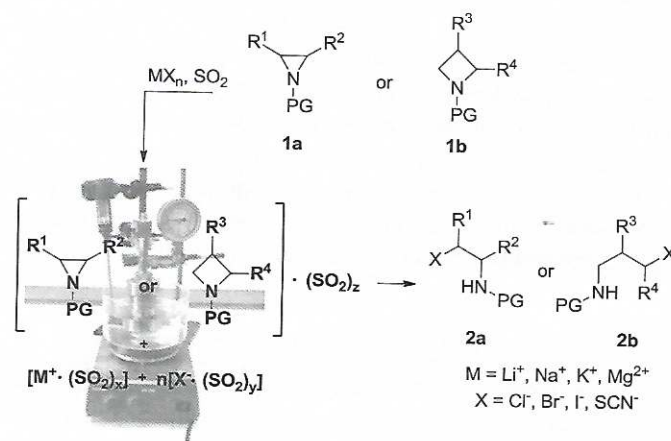
Halogen nucleophiles can be introduced under acidic conditions (e.g.: with HCl) [7]. Another source of halogen nucleophiles are metal halides. However, there are only a few precedents of ring opening using I and II – group metal halides [8].

## RESULTS AND DISCUSSIONS

Here we present a new synthetic process of aziridine and azetidine NRORs with metal halides and other nucleophiles in liquid sulfur dioxide. It is thought that Lewis acid nature of SO<sub>2</sub> activates carbamate protected aziridines and azetidines to the halide attack. Additionally, inorganic salts are soluble in liquid SO<sub>2</sub>.

Our reactions were carried out in three temperature modes: 1) low temp. (-70 °C – -10 °C); 2) ambient temp. (20 °C) and 3) elevated temp. (60 °C – 80 °C). The efficiency of each aziridine or azetidine ring opening reaction was monitored in several solvents in parallel experiments: SO<sub>2</sub>(liq.), DMSO, MeCN, TFE. We have used I and II group metal halides as a source of nucleophile (Scheme 1).

The obtained results showed that the NRORs of aza-heterocycles in liquid sulfur dioxide occur noticeably faster and cleaner than in other solvents.



Scheme 1. Nucleophilic ring opening of azetidine and aziridine with metal halides.

It is important to note that the reactivity of halides is not the only advantage of SO<sub>2</sub> as the solvent. We have found that both starting materials and reaction products are more stable in liquid sulfur dioxide than in DMSO and MeCN.

Obtained results clearly demonstrate that SO<sub>2</sub> is remarkable solvent for NROR's of aziridines and azetidines.

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## REFERENCES

- [1] a) Lugiņina, J. *Synlett* 2014, 25, 2962-2963. b) Deeming, A. S.; Emmett, E. J.; Richards-Taylor, C. S.; Willis, M. C. *Synthesis* 2014, 46, 2701-2710.
- [2] a) Padwa, A.; Woolhouse, A. D. *Comprehensive Heterocyclic Chemistry*, Vol.7, (Ed. W. Lwowski), Pergamon: Oxford, 1984, pp 47-93. b) Tanner, D. *Angew. Chem. Int. Ed. Engl.*, 1994, 33, 559-619. c) Dureault, A.; Tranchepain, I.; Depezay, J. C. *J. Org. Chem.* 1989, 54, 5324-5330. d) Ghorai, M. K.; Kumar, A.; Tiwar, D. P. *J. Org. Chem.* 2010, 75, 137-151.
- [3] Tanner, D.; He, H. M. *Tetrahedron* 1992, 48, 6079-6086.
- [4] Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *J. Org. Chem.* 1990, 55, 4683-4687.
- [5] McCoull, W.; Davis, F. A. *Synthesis* 2000, 1347-1365.
- [6] Legters, J.; Thijs, L.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* 1992, 11, 16-21.
- [7] a) Righi, G.; Potini, C.; Bovicelli, P. *Tetrahedron Lett.* 2002, 43, 5867-5869. b) Righi, G.; Franchini, T.; Bonini, C. *Tetrahedron Lett.* 1998, 39, 2385-2388.
- [8] a) Florio, S.; Luisi, R. *Chem. Rev.* 2010, 110, 5128-5157. b) Lu, P.; *Tetrahedron* 2010, 66, 2549-2560. c) Hu, X. E. *Tetrahedron* 2004, 60, 2701-2743.