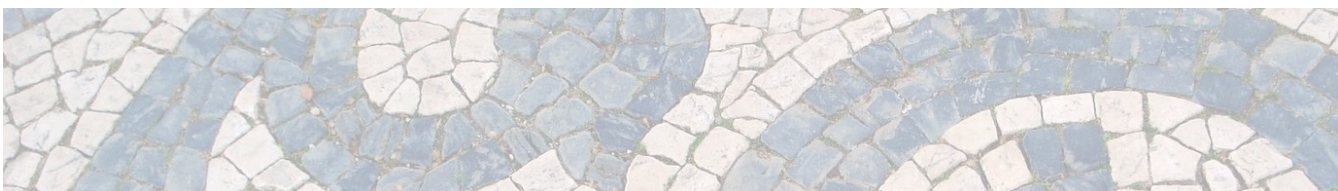


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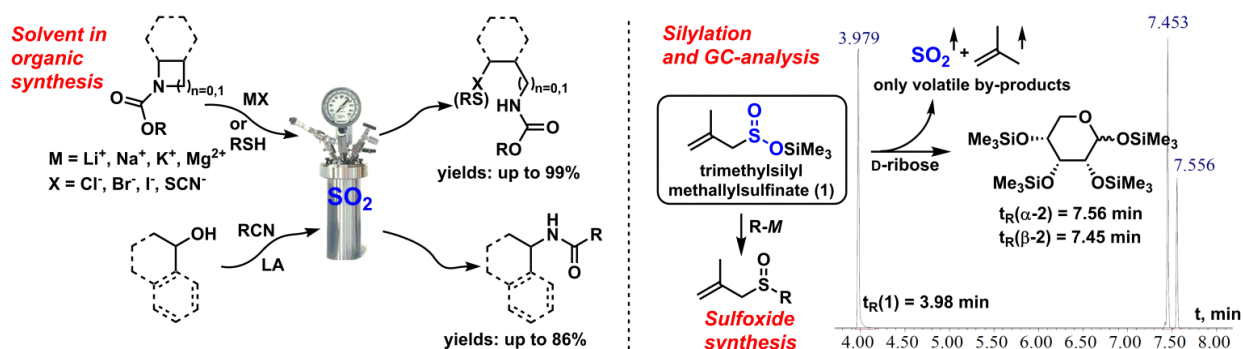
NOVEL APPLICATIONS OF SULFUR DIOXIDE IN ORGANIC AND ANALYTICAL CHEMISTRY

Māris Turks,* Jevgeņija Lugiņina, Daniels Posevins, Agnese Stikute, Irina Novosjolova, Vilnis Peipiņš and Viktors Kumpinsh

Faculty of Material Science and Applied Chemistry, Riga Technical University, P. Valdena Str. 3, Riga, LV-1007, Latvia; maris_turks@ktf.rtu.lv

Sulfur dioxide, which is a gas at ambient conditions, reveals a rather long liquid range: it boils at $-10\text{ }^{\circ}\text{C}$ and freezes at $-75.5\text{ }^{\circ}\text{C}$. Most importantly, SO_2 condenses easily by compression due to its high critical temperature ($157.35\text{ }^{\circ}\text{C}$, 7.88 MPa) and its phase diagram predicts only $\sim 10\text{ atm}$ pressure at $60\text{ }^{\circ}\text{C}$ in a closed reactor.^[1] Sulfur dioxide has a high dipole moment (1.61 D), therefore it readily can dissolve both organic and inorganic salts. On the other hand, SO_2 has been reported as reaction medium for processes involving carbenium ions.^[2]

This has prompted us to search for organic reactions that would profit from their running in liquid SO_2 as a reaction medium.^[3] We have discovered that carbamate-protected aziridines and azetidines undergo efficient ring-opening reactions in liquid SO_2 with I and II group metal halides, including NaCl and KBr (Scheme 1). The advantage of this approach is based on the fact that carbamate groups (Cbz, Boc) can be easier removed if required than their well-described sulfonamide counterparts. We have also found application of liquid SO_2 as an interesting solvent for the Ritter reactions.^[4] The screening of suitable Lewis acid catalysts and scope and limitations of amidation reaction under these conditions will be discussed.



Scheme 1

Additionally, we have developed a method of derivatization of polyhydroxy compounds via silylation and subsequent GC-analysis by Vogel's silyl sulfinate (1) which is obtained in sila-ene reaction between methallylsilane and SO_2 .^[5] This reagent easily transfers the silyl group and forms only volatile by-products: isobutylene and SO_2 . Moreover, the reactions of silyl sulfonates with organometallic reagents providing a direct entry in sulfoxide synthesis will be discussed. This opens a novel approach for allylsulfoxide synthesis from allylsilanes via the sila-ene reaction of the latter with SO_2 followed by addition of Grignard reagents.

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