Organic Synthesis Involving Sulfur Dioxide as Solvent and Reagent

Turks M., Luginina J., Stikute A., Posevins D., Novosjolova I., Peipins V., Suta K., Purins M.

Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena Str. 3, LV-1048, Riga, Latvia
E-mail: maris_turks@ktf.rtu.lv

Sulfur dioxide, which is a gas at ambient conditions, reveals a rather long liquid range: it boils at -10 °C and freezes at -75.5 °C. Most importantly, SO₂ condenses easily by compression due to its high critical temperature (157.35 °C, 7.88 MPa) and its phase diagram predicts only ~10 atm pressure at 60 °C in a closed reactor. Sulfur dioxide has a high dipole moment (1.61 D), therefore it readily can dissolve both organic and inorganic salts. On the other hand, SO₂ has been reported as reaction medium for processes involving carbenium ions.

This has prompted us to search for organic reactions that would profit from their running in liquid SO₂ as a reaction medium [1]. We have discovered that carbamate-protected aziridines and azetidines undergo efficient ring-opening reactions in liquid SO₂ with I and II group metal halides, including NaCl and KBr [2]. 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 SO₂ as an interesting solvent for the Ritter reactions [3]. The screening of suitable Lewis acid catalysts and scope and limitations of amidation reaction under these conditions will be discussed.

Additionally, we have optimized the synthesis of trialkylsilyl methallylsulfimates from sulfur dioxide and the corresponding methallylsilanes and successfully applied them in a traceless silylation of alcohols, polyols and hydroxy carboxylic acids [4]. The developed methodology is applicable for both qualitative and quantitative GC analysis of thermally unstable and nonvolatile compounds. Furthermore trialkylsilyl methallylsulfimates can be used as starting materials in sulfoxide synthesis [4c].

References

This work was supported by the Latvian Council of Science Grant No 12.0291.