SYNLETT Spotlight

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Sulfur Dioxide in the Past Decade

Compiled by Jevgenija Lugina

Jevgenija Lugina was born in 1988 in Daugavpils, Latvia. She studied chemistry at Riga Technical University (RTU) where she obtained her Master degree in chemical engineering in 2013. She is currently working towards her Ph.D. under supervision of Professor Maris Turks at RTU. Her research focuses on reactions of organic compounds in liquid sulfur dioxide.

Faculty of Material Science and Applied Chemistry, Riga Technical University, Paula Valdena Str. 3, Riga, LV-1007, Latvia
E-mail: Jevgenija.Luginina@rtu.lv

Introduction

During the last decade since the previous spotlight on the same reagent, the use of sulfur dioxide increased noticeably. More than 70 articles and patents about sulfur dioxide are published per year. It is widely used in biological research, synthesis of copolymers, radical chemistry, and food processing. However, the most innovative applications are found in synthetic organic chemistry as solvent and reagent.

Abstracts

(A) Lithium sulfinates 2 can be easily prepared from the reaction of organo-lithium compounds 1 with sulfur dioxide. Sulfonylbenzotriazole 3, arising from 2 and 1-chlorobenzotriazole, can be further transformed to sulfonylzides and sulfonamides. Reaction of diaryliodonium salts and 2 gives sulfones. Desulfinylative palladium-catalyzed cross-coupling reaction of 2 with aryl bromides leads to products. Treatment of sulfinate 2 with S8 followed by benzyla-cation afforded s-benzyl alkylthiosulfonates.

(B) Recently, Vogel and co-workers reported a convenient and practical method for the synthesis of sulfinic Lewis acid complex that can be further converted into a range of sulfinyl or sulfonyl derivatives. Chlorination of 8 with NCS yields sulfonyl chloride that can be easily transformed into sulfonamides and sulfonic esters. Also sulfinic acid silyl and alkyl esters and sulfones can be obtained from 8.

(C) Turks et al. reported a method for the synthesis of allylsulfoxides from and Grignard reagents. The mixed anhydride 14 was generated in situ from prop-2-ene-1-boronate and sulfur dioxide. The potent nanomolar α-L-fucosidase inhibitor can be synthesized via the reaction of SO2 with the D-ribose-derived nitrone. Addition of SO2 to 16 initiates a reaction sequence which involves formation of 18 as an intermediate via cleavage of the N–O bond and acetonide hydrolysis. Subsequent hydrogensulfite addition onto imine forms crystalline intermediate. Further desulfonation of 17 in the presence of barium hydroxide provided amino sugar.
(E) The synthetic advances on Vogel’s cascade, which starts with the hetero-Diels–Alder addition between dienes and SO₂, led to efficient synthesis of chiral cyclopentene and cyclohexene various δ-lactones and the first total synthesis of (−)-dolabriferol.

(F) Toste and co-workers reported a method for the SO₂ insertion into an Au–C bond. The resulting complex proved to be the key intermediate for an unprecedented synthesis of sulfones and sulfonamides from arylboronic acids and SO₂ or its precursor K₂SO₄.

(G) Recently, a stable complex of DABCO and SO₂ was obtained and used as sulfur dioxide transfer reagent. DABSO has the same electrophilic trapping of metal sulfinates and used as sulfur dioxide transfer reagent. DABSO has the same utilities affording chiral sulfone intermediate for an unprecedented synthesis of sulfones and sulfonamides from arylboronic acids and SO₂ or its precursor K₂SO₄.

References