SYNLETT Spotlight

Sulfur Dioxide in the Past Decade

Compiled by Jevgenija Lugiņina

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

Jevgenija Lugiņina 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,¹ the use of sulfur dioxide increased noticeably. More than 70 articles and patents about sulfur diox-

ide are published per year. It is widely used in biological research, synthesis of copolymers,² radical chemistry,³ and food processing. However, the most innovative applications are found in synthetic organic chemistry as solvent⁴ and reagent.⁵

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 sulfonylazides and sulfonamides.⁶ Reaction of diaryliodonium salts and **2** gives sulfones **4**.⁷ Desulfinylative palladium-catalyzed cross-coupling reaction of **2** with aryl bromides leads to products **5**.⁸ Treatment of sulfinates **2** with S_8 followed by benzylation afforded *S*-benzyl alkylthiosulfonates **6**.^{9,10}

(B) Recently, Vogel and co-workers¹¹ reported a convenient and practical method for the synthesis of sulfinic Lewis acid complex **8** that can be further converted into a range of sulfinyl or sulfonyl derivatives. Chlorination of **8** with NCS yields sulfonyl chloride **9** that can be easily transformed into sulfonamides and sulfonic esters. Also sulfinic acid silyl (**10**) and alkyl esters **11** and sulfones **12** can be obtained from **8**.

(C) Turks et al. reported a method for the synthesis of allylsulfoxides **15** from **14** and Grignard reagents. The mixed anhydride **14** was generated in situ from prop-2-ene-1-boronate **13** and sulfur dioxide.¹²

(D) The potent nanomolar α -L-fucosidase inhibitor **18** can be synthesized via the reaction of SO_2 with the D-ribose-derived nitron **16**. Addition of SO_2 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 **17**. Further desulfonation of **17** in the presence of barium hydroxide provided amino sugar **18**.¹³

(E) The synthetic advances on Vogel's cascade,^{5c} which starts with the hetero-Diels–Alder addition between dienes **19** and SO₂, led to efficient synthesis of chiral cyclopentene **22** and cyclohexenone **23**,¹⁴ various δ -lactones **25**,¹⁵ and the first total synthesis of (–)-dolabriferol.¹⁶

(F) Toste and co-workers reported a method for the SO₂ insertion into a Au–C bond. The resulting complex **27** proved to be the key intermediate for an unprecedented synthesis of sulfones and sulfonamides from arylboronic acids and SO₂ or its precursor K₂S₂O₅.¹⁷

(G) Recently, a stable complex of DABCO and SO₂ was obtained and used as sulfur dioxide transfer reagent.¹⁸ DABSO has the same reactivity as gaseous SO₂ but excludes most of the hazards associated with it. Electrophilic trapping of metal sulfinates **29** with epoxides affording chiral sulfone **30** is an example for the wide range of DABSO application as sulfur dioxide donor.¹⁹

References

- (1) Fonquerne, F. *Synlett* **2005**, 1340.
- (2) (a) Tanaka, N.; Sato, E.; Matsumoto, A. *Macromolecules* **2011**, *44*, 9125. (b) Takenaka, Y.; Kiyosu, T.; Mori, G.; Choi, J. C.; Fukaya, N.; Sakakura, T.; Yasuda, H. *ChemSusChem* **2012**, *5*, 194.
- (3) Koshechko, V. G.; Kiprianova, L. A.; Kalinina, L. I. *J. Fluorine Chem.* **2009**, *130*, 317.
- (4) (a) Schmidt, D.; Leutbecher, H.; Conrad, J.; Klaiber, I.; Mika, S.; Greiner, G.; Beifuss, U. *Synlett* **2007**, 1725. (b) Deeming, A. S.; Emmett, E. J.; Richards-Taylor, C. S.; Willis, M. C. *Synthesis* **2014**, *46*, 2701.
- (5) (a) Vogel, P.; Turks, M.; Bouchez, L.; Craita, C.; Huang, X.; Murcia, M. C.; Fonquerne, F.; Didier, C.; Flowers, C. *Pure Appl. Chem.* **2008**, *80*, 791. (b) Lavigne, F.; Maerten, E.; Alcaraz, G.; Branchadell, V.; Saffon-Merceron, N.; Baccaredo, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 2489. (c) Vogel, P.; Turks, M.; Bouchez, L.; Marković, D.; Varela-Álvarez, A.; Sordo, J. Á. *Acc. Chem. Res.* **2007**, *40*, 931. (d) Vogel, P.; Marković, D.; Turks, M. *Sulfur Dioxide: A Powerful Tool for the Stereoselective Construction of C–C Bonds*, In *Stereoselective Synthesis of Drugs and Natural Products*, Chap. 22; Andrushko, V.; Andrushko, N., Eds.; John Wiley & Sons: Hoboken, New Jersey, **2013**, 623.
- (6) (a) Katritzky, A.; Widyana, K.; Gyanda, K. *Synthesis* **2008**, 1201. (b) Teague, S. J.; Barber, S. *Tetrahedron Lett.* **2010**, *51*, 4720. (c) Luckhurst, C. A.; Millichip, I.; Parker, B.; Reuberson, J.; Furber, M. *Tetrahedron Lett.* **2007**, *48*, 8878.
- (7) Umierski, N.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 4972.
- (8) (a) Sévigny, S.; Forgione, P. *New J. Chem.* **2013**, *37*, 589. (b) Sévigny, S.; Forgione, P. *Chem. Eur. J.* **2013**, *19*, 2256.
- (9) Kim, S.; Lim, K. C.; Kim, S. *Chem. Asian J.* **2008**, *3*, 1692.
- (10) Pandya, R.; Murashima, T.; Tedeschi, L.; Barrett, A. G. M. *J. Org. Chem.* **2003**, *68*, 8274.
- (11) (a) Marković, D.; Volla, C. N. R.; Vogel, P.; Varela-Álvarez, A.; Sordo, J. A. *Chem. Eur. J.* **2010**, *16*, 5969. (b) Volla, C. M. R.; Dubbaka, S. R.; Vogel, P. *Tetrahedron* **2009**, *65*, 504. (c) Volla, C. M. R.; Marković, D.; Dubbaka, S. R.; Vogel, P. *Eur. J. Org. Chem.* **2009**, 6281. (d) Zambroń, B. K.; Dubbaka, S. R.; Marković, D.; Moreno-Clavijo, E.; Vogel, P. *Org. Lett.* **2013**, *15*, 2550.
- (12) Turks, M.; Lawrence, A. K.; Vogel, P. *Tetrahedron Lett.* **2006**, *47*, 2783.
- (13) Chevrier, C.; Le Nouen, D.; Defoin, A.; Tarnus, C. *Carbohydr. Res.* **2011**, *346*, 1202.
- (14) Turks, M.; Vogel, P. *J. Org. Chem.* **2009**, *74*, 435.
- (15) Exner, C. J.; Laclef, S.; Poli, F.; Turks, M.; Vogel, P. *J. Org. Chem.* **2011**, *76*, 840.
- (16) Laclef, S.; Turks, M.; Vogel, P. *Angew. Chem. Int. Ed.* **2010**, *49*, 8525.
- (17) Johnson, M. W.; Bagley, S. W.; Mankad, N. P.; Bergman, R. G.; Mascitti, V.; Toste, F. D. *Angew. Chem. Int. Ed.* **2014**, *53*, 4404.
- (18) Martial, L. *Synlett* **2013**, *24*, 1595.
- (19) (a) Bisserset, P.; Blanchard, N. *Org. Biomol. Chem.* **2013**, *11*, 5393. (b) Demming, A. S.; Russel, C. J.; Hennessy, A. J.; Willis, M. C. *Org. Lett.* **2014**, *16*, 150. (c) Rocke, B. N.; Bahnck, K. B.; Herr, M.; Laverne, S.; Mascitti, V.; Perreault, C.; Polivkova, J.; Shavnya, A. *Org. Lett.* **2014**, *16*, 154.