

SYNLETT Spotlight

Sulfur Dioxide in the Past Decade

Compiled by Jevgeņija Lugiņina



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

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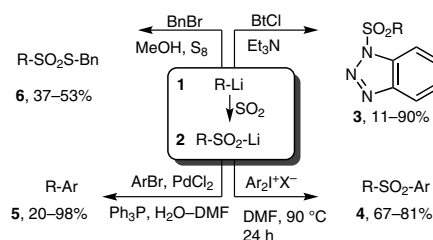
Introduction

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-

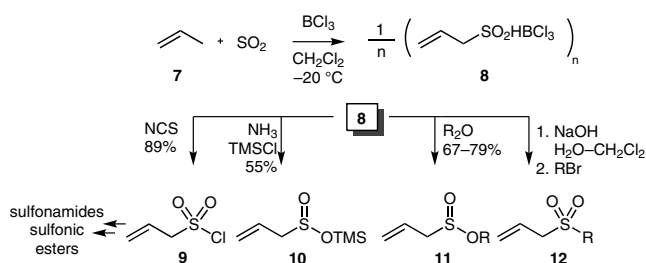
ide are published per year. It is widely used in biological research, synthesis of copolymers,² radical chemistry,³ and food processing. However, the most innovative applications are found in synthetic organic chemistry as solvent⁴ and reagent.⁵

Abstracts

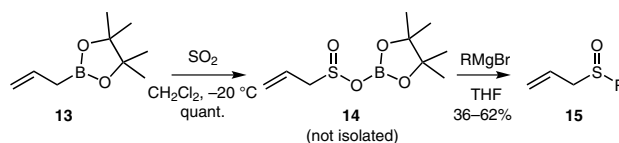
(A) Lithium sulfinates **2** can be easily prepared from the reaction of organo-lithium compounds **1** with sulfur dioxide. Sulfonylbenzotriazole **3**, arising from **2** and 1-chlorobenzotriazole, can be further transformed to sulfonylazides and sulfonamides.⁶ Reaction of diaryliodonium salts and **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 S₈ followed by benzylation afforded *S*-benzyl alkylthiosulfonates **6**.^{9,10}



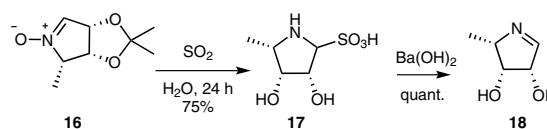
(B) Recently, Vogel and co-workers¹¹ reported a convenient and practical method for the synthesis of sulfinic Lewis acid complex **8** that can be further converted into a range of sulfinyl or sulfonyl derivatives. Chlorination of **8** with NCS yields sulfonyl chloride **9** that can be easily transformed 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 SO₂ with the D-ribose-derived nitron **16**. 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 acetone 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



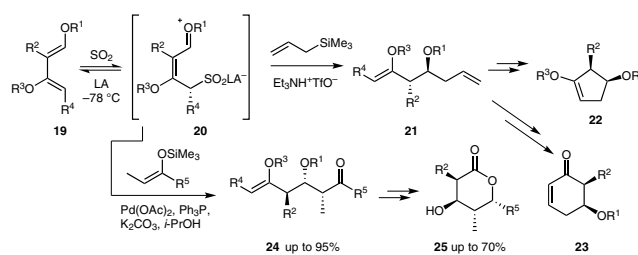
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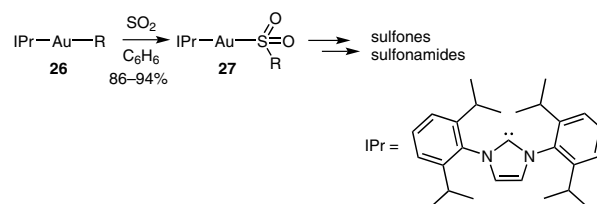
DOI: 10.1055/s-0034-1379460; Art ID: st-2014-v0499-v

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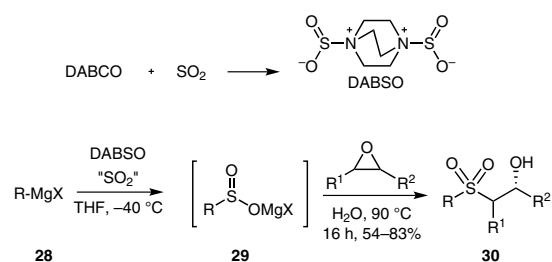
(E) The synthetic advances on Vogel's cascade,^{5c} which starts with the hetero-Diels–Alder addition between dienes **19** and SO₂, led to efficient synthesis of chiral cyclopentene **22** and cyclohexenone **23**,¹⁴ various δ -lactones **25**,¹⁵ and the first total synthesis of (–)-dolabriferol.¹⁶



(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



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