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

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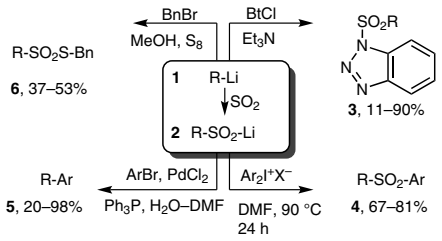
Introduction

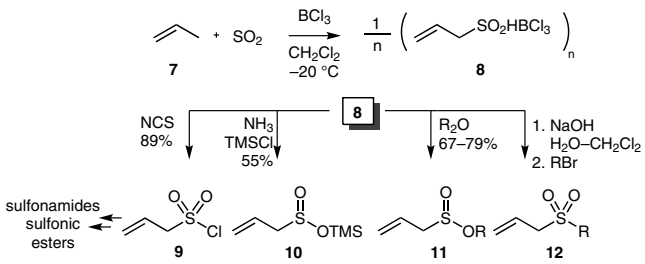
During the last decade since the previous spotlight on the same reagent,[1] the use of sulfur dioxide increased noticeably. More than 70 articles and patents about sulfur dioxide are published per year. It is widely used in biological research, synthesis of copolymers,[2] radical chemistry,[3] and food processing. However, the most innovative applications are found in synthetic organic chemistry as solvent[4] and reagent.[5]

Abstracts

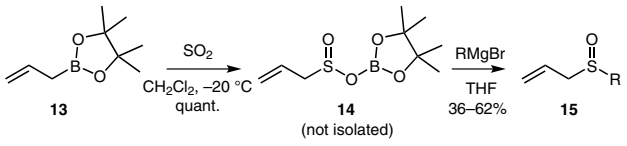
(A) Lithium sulfinates **2** can be easily prepared from the reaction of organo-lithium compounds **1** with sulfur dioxide. Sulfonylbenzotriazole **3**, arising from **2** and 1-chlorobenzotriazole, can be further transformed to sulfonylazides and sulfonamides.[6] Reaction of diaryliodium salts and **2** gives sulfones **4**.[7] Desulfinylative palladium-catalyzed cross-coupling reaction of **2** with aryl bromides leads to products **5**.[8] Treatment of sulfinate **2** with S_8 followed by benzylation afforded *S*-benzyl alkylthiosulfonates **6**.[9,10]



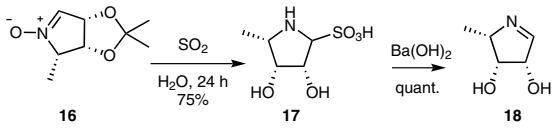
(B) Recently, Vogel and co-workers[11] reported a convenient and practical method for the synthesis of sulfinic Lewis acid complex **8** that can be further converted into a range of sulfinyl or sulfonyl derivatives. Chlorination of **8** with NCS yields sulfonyl chloride **9** that can be easily transformed 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 nitrone **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]



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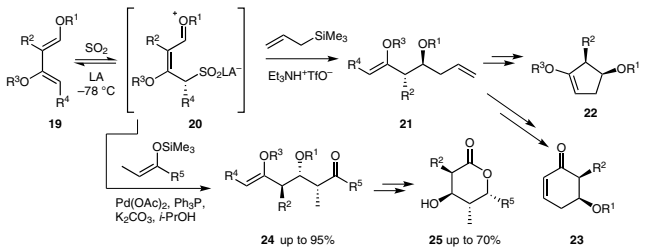
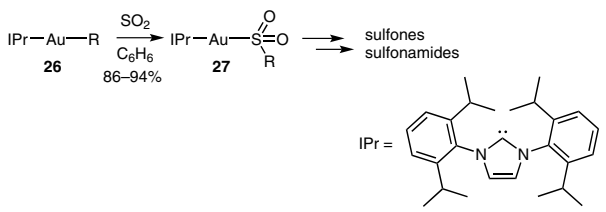
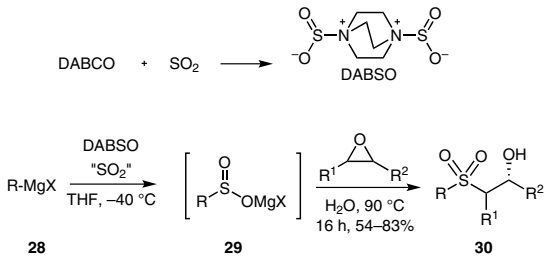
(E) The synthetic advances on Vogel's cascade,[5c] which starts with the hetero-Diels–Alder addition between dienes **19** and SO_2, led to efficient synthesis of chiral cyclopentene **22** and cyclohexenone **23**,[14] various δ-lactones **25**,[15] and the first total synthesis of (–)-dolabriferol.[16]



(F) Toste and co-workers reported a method for the SO_2 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 SO_2 or its precursor $K_2S_2O_5$.[17]



(G) Recently, a stable complex of DABCO and SO_2 was obtained and used as sulfur dioxide transfer reagent.[18] DABSO has the same reactivity as gaseous SO_2 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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