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 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 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 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 2-ribose-derived nitrone 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 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,\(^{26}\) which starts with the hetero-Diels–Alder addition between dienes \(19\) and \(\text{SO}_2\), led to efficient synthesis of chiral cyclopentene \(22\) and cyclohexenone \(23,\)\(^{24}\) various \(\delta\)-lactones \(25,\)\(^{18}\) and the first total synthesis of \((-)\)-dolabriferol.\(^{16}\)

(F) Toste and co-workers reported a method for the \(\text{SO}_2\) insertion intermediate for an unprecedented synthesis of sulfones and sulfonamides from aryloboronic acids and \(\text{SO}_2\) or its precursor \(\text{K}_2\text{S}_2\text{O}_7.\)\(^{21}\)

(G) Recently, a stable complex of DABCO and \(\text{SO}_2\) was obtained and used as sulfur dioxide transfer reagent.\(^{19}\) DABSO has the same reactivity as gaseous \(\text{SO}_2\) but excludes most of the hazards associated with it. Electrophilic trapping of metal sulfinates with epoxides affording chiral sulfone \(30\) is an example for the wide range of DABSO application as sulfur dioxide donor.\(^{19}\)

References

(1) Fonquerme, F. Synlett 2005, 1340.