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 diaryliodide 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 benzyla- tion 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 β-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 acetoni de 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
Recently, a stable complex of DABCO and SO$_2$ was obtained by Toste and co-workers. This complex can be used as a sulfur dioxide donor for the synthesis of sulfones and sulfamides from arylboronic acids and SO$_2$ or its precursor K$_2$S$_2$O$_5$. DABSO has the same reactivity as gaseous SO$_2$ but excludes most of the hazards associated with it. Electrophilic trapping of metal sulfinates has led to the use of DABSO in the application as sulfur dioxide donor.