SYNLETT Spotlight 121

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

Sulfur Dioxide

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Dedicated to my father

Introduction

Sulfur dioxide, obtained by burning sulfur in air, is a useful and suitable solvent and reagent for a large number of reactions.^{1,2} It has a broad liquid range (mp $-75\text{ }^{\circ}\text{C}$ and bp $-10\text{ }^{\circ}\text{C}$), a comparably high solvation power for both ionic and covalent compounds, and low nucleophilicity.

It is also a Lewis acid that is able to complex unsaturated organic compounds. Recently, this reagent has been used in the synthesis of long chain polyketides,³ sulfones, sulfinates, sulfonamides, and methanesulfonic acid.

Abstracts

(A) Alkenes are isomerized by sulfur dioxide. The process is generally explained by invoking an ene reaction between an SO_2 molecule and the alkene.⁴ Recently, Vogel et al. revised this mechanism⁵ and showed that polysulfones resulting from the copolymerization of alkenes and SO_2 catalyze the reaction. This has led to the development of a new method for the selective cleavage of methyl-substituted allyl ethers under neutral conditions.⁶

(B) Methane is transformed selectively to methanesulfonic acid at low temperature by liquid-phase sulfonation of methane with SO_2 and O_2 in the presence of Pd salts and Cu salts⁷ as the catalysts or of CaO as promoter.⁸

(C) Irradiation of *N*-hydroxy-2-thiopyridone esters with visible light in the presence of sulfur dioxide gives the corresponding thio-sulfonates. These can be converted into sulfones by treatment with KOH and an alkylating agent.⁹

(D) 1,3-Dienes undergo hetero Diels–Alder reactions with SO_2 at low temperature in the presence of an acid promoter, such as $\text{CF}_3\text{CO}_2\text{H}$ or $\text{BF}_3\cdot\text{Et}_2\text{O}$, leading to sultines.¹⁰

(E) Allyl tin derivatives undergo ene reactions with sulfur dioxide, furnishing tin allyl sulfonates.¹¹ Recently, it was shown that allylsilanes and enoxysilanes derived from aldehydes, ketones and esters also produce ene adducts with SO₂.¹² The silyl sulfonates from ene reactions can be brominated (Br₂ or NBS) or chlorinated (Cl₂ or NCS) to produce the corresponding sulfonyl halides. The latter react with primary or secondary amines or alcohols to give the corresponding sulfonamides or sulfonic esters (one-pot, three-component syntheses).¹³

(F) Sultines **2**, arising from HDA reactions between dienes **1** and SO₂, can be quenched with carbon nucleophiles such as enoxysilanes or allylsilanes to give silylsulfonates **4**. Desilylation of **4** and reaction with carbon electrophiles generates polyfunctional sulfones in one-pot, four-component operations.¹⁴ Alternatively, **4** can be oxidized with NCS and reacted with amines or alcohols to produce polyfunctional sulfonamides **6** or sulfonic esters **7**, containing up to three stereogenic centers. Hydrolysis of silyl sulfonates **4** and subsequent desulfuration generates polyketides and analogs **8**, also in one-pot operations.¹⁵

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