Sulfur Dioxide
Compiled by Freddy Fonquerne

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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.\textsuperscript{1,2} It has a broad liquid range (mp $-75^\circ$C and bp $-10^\circ$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,\textsuperscript{3} sulfones, sulfinites, 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\textsubscript{2} molecule and the alkene.\textsuperscript{4} Recently, Vogel et al. revised this mechanism\textsuperscript{5} and showed that polysulfones resulting from the copolymerization of alkenes and SO\textsubscript{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.\textsuperscript{6}

\[
\begin{align*}
\text{CH}_2 + \text{SO}_2 + 1/2 \text{O}_2 & \xrightarrow{\text{Pd and Cu salts or CaO promoters}} \text{CH}_3\text{SO}_2\text{H} \\
\text{O} & \text{N}  \\
\text{S} & \\
\text{light} & \\
\text{SO}_2 & \xrightarrow{\text{KOH, R'X}} \text{RSO}_2\text{SPy} \\
\text{R} & = \text{R'} = \text{Alkyl} \\
\end{align*}
\]

(B) Methane is transformed selectively to methanesulfonic acid at low temperature by liquid-phase sulfonation of methane with SO\textsubscript{2} and O\textsubscript{2} in the presence of Pd salts and Cu salts\textsuperscript{7} as the catalysts or of CaO as promoter.\textsuperscript{8}

\[
\begin{align*}
\text{CH}_4 + \text{SO}_2 + 1/2 \text{O}_2 & \xrightarrow{\text{Pd and Cu salts or CaO promoters}} \text{CH}_3\text{SO}_2\text{H} \\
\end{align*}
\]

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

\[
\begin{align*}
\text{O} & \text{N}  \\
\text{S} & \\
\text{light} & \\
\text{SO}_2 & \xrightarrow{\text{KOH, R'X}} \text{RSO}_2\text{SPy} \\
\text{R} & = \text{R'} = \text{Alkyl} \\
\end{align*}
\]

(D) 1,3-Dienes undergo hetero Diels–Alder reactions with SO\textsubscript{2} at low temperature in the presence of an acid promoter, such as CF\textsubscript{3}CO\textsubscript{2}H or BF\textsubscript{3}Et\textsubscript{2}O, leading to sultines.\textsuperscript{10}

\[
\begin{align*}
\text{Me} + \text{SO}_2 & \xrightarrow{-80^\circ\text{C}} \text{MeSO}_2\text{O} \\
\end{align*}
\]
(E) Allyl tin derivatives undergo ene reactions with sulfur dioxide, furnishing tin allyl sulfinates. Recently, it was shown that allylsilanes and enoxysilanes derived from aldehydes, ketones and esters also produce ene adducts with SO₂. The silyl sulfinates 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).

(F) Sultines, arising from HDA reactions between dienes 1 and SO₂, can be quenched with carbon electrophiles 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. 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.

References

(2) For review see: (a) Tokura, N. Synthesis 1971, 639.