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LETTERS

Trimethylsilylsulfonyl chloride as a source of sulfur trioxide: a novel synthesis of sultones

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Abstract

The reaction of trimethylsilylsulfonyl chloride with iodosobenzene at −78°C generates sulfur trioxide, or a sulfur trioxide precursor that reacts with alkenes to give sultones in good yield. This provides a simple method of preparing sulfur trioxide in situ and avoids the presence of Lewis bases. © 1999 Elsevier Science Ltd. All rights reserved.

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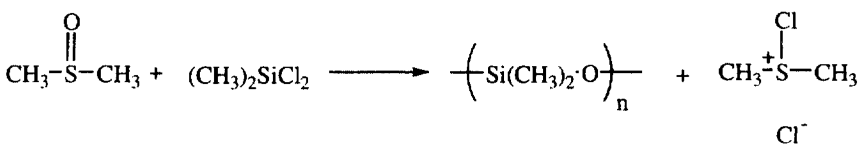
Sultones are usually prepared by the sulfonation of alkenes.[1–3] β-Sultones are the usual product, however, under the reaction conditions they often rearrange to give larger rings.[4,5] Difficulty of handling sulfur trioxide coupled to the need to reduce its electron-acceptor properties has led to the development of numerous Lewis-base complexed sulfur trioxide reagents such as SO_3–dioxane,[6] SO_3–pyridine[7] and SO_3–triethylamine.[8] As part of an ongoing project to prepare silyl substituted small ring heterocycles we needed to prepare sulfur trioxide in situ in the absence of Lewis bases.

Dimethylsulfoxide has been shown to react with chlorosilanes to give siloxanes via a non-aqueous hydrolytic route (Scheme 1).[9,10] The formation of the strong silicon oxygen bond ensures complete formation of the siloxane together with the chlorosulfonium compound.



$$CH_3-\overset{O}{\overset{\|}{S}}-CH_3 + (CH_3)_2SiCl_2 \longrightarrow \left(Si(CH_3)_2 \cdot O \right)_n + CH_3-\overset{Cl}{\overset{|}{S^+}}-CH_3 \; Cl^-$$

Scheme 1.

We have found that other, higher oxidation state compounds behave similarly. Thus, iodosobenzene reacts with dimethyldichlorosilane to give a range of, mainly cyclic, siloxanes together with iodosobenzene dichloride. If the reaction is performed in the presence of anisole, a mixture of 2- and 4-chloroanisole

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is produced, confirming the in situ generation of the iodosobenzene dichloride which subsequently chlorinates the anisole. The corresponding reaction of trimethylsilylsulfonyl chloride with iodosobenzene should generate sulfur trioxide (Scheme 2).

$$PhIO + 2(CH_3)_3SiSO_3Cl \longrightarrow (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + SO_3 + PhCl_2$$

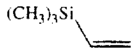
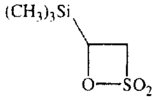
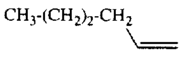
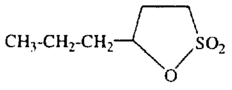
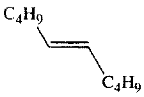
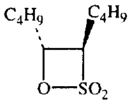
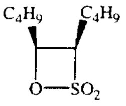
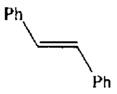
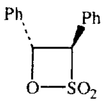
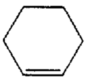
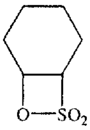
Scheme 2.

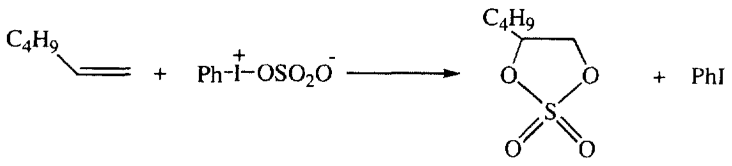
Table 1 displays the results of reacting trimethylsilylsulfonyl chloride with iodosobenzene at −78°C in dry dichloromethane followed by the addition of various alkenes.[11] The corresponding β-sultones are formed in good yield confirming that iodosobenzene reacts with trimethylsilylsulfonyl chloride to generate either sulfur trioxide or a precursor that behaves in a similar fashion. Under the conditions of the reaction, rearrangement was only observed with hex-1-ene, which gave the γ sultone. Analysis of the reaction mixture revealed the only other products to be hydroxysulfonic acid or alkene sulfonic acid derivatives.

Iodosobenzene has been shown to react with sulfur trioxide to give phenyliodosulfate,[12] which can be isolated as a yellow solid. Reaction of this with alkenes gives not the sultone but the corresponding cyclic sulfates in about 80% yield (Scheme 3).

In our studies we found no evidence of cyclic sulfate formation when the alkene is reacted in situ with

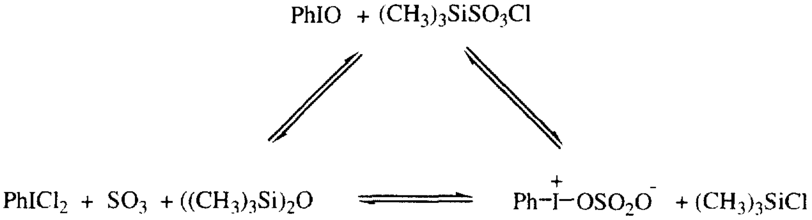
Table 1
Yields of β-sultones obtained from reaction of an alkene with a mixture of iodosobenzene and trimethylsilylsulfonyl chloride

Alkene	Sultone	% yield	Reference
		57	13
		68	14
		65	15
		50	12
		60	16
		69	17



Scheme 3.

iodosobenzene and trimethylsilylsufonyl chloride at –78°C. We suggest that the formation of the strong Si–O bond favours the formation of SO_3 via the equilibria shown in Scheme 4.



Scheme 4.

We are at present examining other reactions of sulfur trioxide, or its precursor, generated by this method.

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11. Synthesis of sultones: To a slurry of iodosobenzene (2.20 g, 0.01 mol) in 50 ml dry dichloromethane, at –78°C under nitrogen atmosphere was added chlorotrimethylsilylsulfonate ester (1.5 ml, 0.01 mol) with continuous stirring to produce a clear yellow solution. To this was added the alkene (1.5 g, 0.015 mol), and the reaction mixture allowed to warm up to room temperature. Stirring was continued at this temperature for a further 1 h, followed by removal of the solvent from the reaction mixture. Purification of the crude product using column chromatography (silica gel with hexane/dichloromethane as the eluent) gave the sultones in the yields quoted in Table 1.
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13. 2-Trimethylsilyl-1,2-ethanesultone is a colourless oil, which readily decomposes after a few hours at room temperature; ^1H NMR (400 MHz, $CDCl_3$) δ=0.22 (s, 9H, $SiMe_3$), 3.88 (dd, 1H, J_1=6.8 Hz, J_2=12.8 Hz, CH_2S) and 4.06 (dd, 1H, J_1=4.4 Hz, J_2=12.8 Hz, CH_2S), 4.9 (m, 1H, $CHOSO_2$-); ^{13}C NMR: (100 MHz, $CDCl_3$) δ=–2.95 ($SiMe_3$), 43.80 (CH_2SO_2O-), 85.79 ($CHOSO_2$-); IR (neat) ν=2957, 2927, 1400, 1254, 1190, 914, 846 cm^{-1}; EIMS *m/e* (%)=181 (5.8) (MH^+), 167 (17), 147 (35), 137 (2.3), 116 (4.5), 101 (23), 93 (37), 73 (100), 59 (13), 45 (28), 29 (3).
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16. *trans*-1,2-Diphenylsultone is a white solid (m.p. 171°C); ^1H NMR (400 MHz, $CDCl_3$) δ=5.22 (s, 1H, CHS), 5.76 (s, 1H, CHO), 7.30–7.45 (m, 10H, 2×Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ=65.69 (CHO), 76.68 (CHS), 128.04, 128.54, 128.99,

138.34 (Ph); IR (KBr) ν=1550, 1475, 1300, 1250, 1200, 1175, 1050, 900, 800, 750, 700, 675, 564, 511 cm^{-1}; EIMS *m/e* (%)=196 (MH$^+$–SO$_2$) (37), 195 (40), 178 (20), 168 (17), 167 (70), 165 (25), 152 (17), 105 (100), 90 (60), 89 (66), 77 (58), 64 (11), 63 (22), 57 (6), 51 (27), 39 (14), 28 (7); Analysis calcd for C$_{14}$H$_{12}$SO$_3$: C 64.6, H 4.7; found: C 65.0, H 4.9.

17. 1,2-Cyclohexanesultone is a colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ=1.42 (m, 2H, -CH_2CHO-), 1.81 (m, 4H, -CH$_2$CH$_2$-), 2.22 and 2.27 (m, 2H, -CH$_2$CHSO$_2$-), 4.04 (m, 1H, CHSO$_2$O-), 4.87 (m, 1H, CHOSO$_2$-); ^{13}C NMR (400 MHz, CDCl$_3$) δ=22.09, 22.70, 29.65, 33.12 (4×CH$_2$), 58.58 (CHSO$_2$O-), 85.97 (CHOSO$_2$-); IR (neat) 3000, 2986, 1470, 1225, 987, 946, 770 cm^{-1}; EIMS *m/e* (%)=162 (M$^+$) (0.6), 98 (M–SO$_2$) (5), 81 (100), 80 (49), 79 (25), 77 (8), 75 (6), 67 (15), 57 (15), 41 (29), 39 (14), 29 (9), 27 (11); Analysis calcd for C$_6$H$_{10}$SO$_3$: C 44.4, H 6.2; found: C 44.7, H 6.1.