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Synthesis of 4-Methyl-1,2-oxathiin 2,2-Dioxide

Tetsuo Akiyama, Masaki Sugihara, Takeshi Imagawa, and Mituyosi Kawanisi
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606

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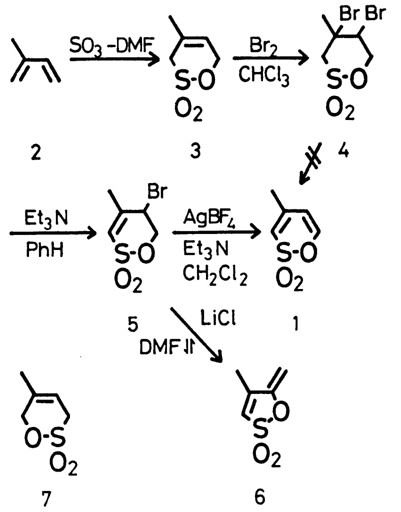
Synopsis. The reaction of isoprene with the SO_3–DMF complex afforded isoprene δ-sultone (**3**) in a 48% yield. The addition of bromine to **3** gave a dibromo product (**4**) and successive treatment of **4** with triethylamine in benzene and with triethylamine in the presence of silver tetrafluoroborate gave 4-methyl-1,2-oxathiin 2,2-dioxide in an 18% yield.

A δ-sultone, 1,2-oxathiin 2,2-dioxide is a structurally interesting compound since it is equivalent to 2-pyrone, the C=O group of which is replaced by a sulfonyl group (SO_2). In addition, 1,2-oxathiin 2,2-dioxides, which readily release sulfur dioxide to give furans,[1] can be regarded as potential starting materials for the synthesis of furan derivatives. From the viewpoint of synthesis, the 1,2-oxathiin 2,2-dioxides which have one substituent at the 4 or 5 position appear to be useful in the preparation of 3-substituted furans.[2] In the present paper, the first synthesis of 4-methyl-1,2-oxathiin 2,2-dioxide (**1**) is reported.

Up to the present time, no preparations of 1,2-oxathiin 2,2-dioxide and its monosubstituted derivatives, except the 6-substituted derivative[3] have been reported. Even in this case, the detailed method of preparation was not reported. The reaction sequence is depicted in the following scheme.



Scheme 1.

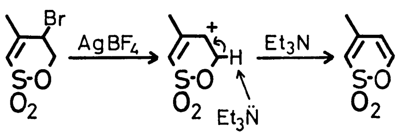
To the best of the authors' knowledge, only a few cases of successful formation of six-membered δ-sultones by way of the cycloaddition of SO_3 with a 1,3-diene are known,[4] although the reactions between SO_3 and olefinic compounds have been widely investigated.[5]

The reaction of isoprene (**2**) with the SO_3-*N*,*N*-dimethylformamide (DMF) complex[4a] was attempted and isoprene δ-sultone (**3**) was obtained as the sole product, in a 48% yield. The structure of **3** was differentiated from that of the alternate, **7**, in view of the fact that the methylene protons adjacent to the SO_2 group exhibited a broad singlet peak and did not couple with the olefinic proton in the ^1H-NMR spectra. This was further confirmed by chemical transformation (*vide infra*).

Similarly, 2,3-dimethyl-1,3-butadiene gave a δ-sultone (18% yield), but none of these products was formed in the case of 1,3-butadiene, 1,3-pentadiene and 1,3-cyclohexadiene. The reaction between SO_3 and 1,3-butadiene following a published procedure[5b] gave a δ-sultone, but the yield was extremely low.

The addition of bromine to isopren δ-sultone (**3**) in a chloroform solution afforded the corresponding dibromo derivative (**4**: 91%). Treatment of **4** with triethylamine in benzene induced monodehydrobromination giving **5** (95%). The additional treatment of **5** with bases, such as pyridine or potassium *t*-butoxide, in addition to triethylamine failed to produce a dienic compound. However, dehydrobromination of **5** by means of lithium chloride and calcium carbonate in refluxing *N*,*N*-dimethylformamide afforded a dienic compound in a 60% yield the structure of which was found to be 4-methyl-5-methylene-1,2-oxathiole 2,2-dioxide (**6**) from elemental analysis and spectral data. The formation of the ring-contracted product (**6**) is intriguing, but the true mechanism is not known as yet.

The following procedure gave the target compound, (**1**). Thus, treatment of **5** with triethylamine in dichloromethane in the presence of silver tetrafluoroborate gave **1** in an 18% yield. Support for this structural assignment comes from ^1H- and ^{13}C-NMR spectra. The signals of protons at C_5 and C_6 in the ^1H-NMR spectra display a typical AX pattern ($J=5.9$ Hz) and the ^{13}C-NMR spectra show that three olefinic carbons at the 3, 5, and 6 positions attach to one proton, respectively. The reaction appears to proceed as in the following scheme.



Scheme 2.

Experimental

All temperatures are uncorrected. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The mass spectra were taken using a Hitachi RMS-4 mass spectrometer. The NMR spectra were obtained on Varian EM-360 and CFT-20 spectrometers, TMS being chosen as the internal standard.

Isoprene δ-Sultone (3). To a solution of SO_3 (13.3 g; 0.166 mol) in 60 ml of DMF were added 10.0 g (0.147 mol) of isoprene all at once at room temperature. After the slightly exothermic reaction subsided within about one-half hour, the reaction mixture was stirred for 24 h at room temperature and neutralized with cold $NaHCO_3$ aq and extracted with benzene. The extract was washed with water to remove DMF and dried (Na_2SO_4). After removal of the solvent *in vacuo*, the residue slowly crystallized. Recrystallization from EtOH gave 10.5 g (48.0%) of 4-methyl-3,6-dihydro-1,2-oxathiin 2,2-dioxide (**3**), mp 35—36 °C; MS: *m/e* 148 (M^+, 21%); IR (Nujol): 1180, 1360 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 5.54 (m, 1H, -CH=), 4.83 (m, 2H, OCH_2), 3.58 (broad s, 2H, CH_2SO_2), 1.83 ppm (broad s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$): δ 128.2 (>C=), 117.2 (=CH-), 71.5 (CH_2O), 50.1 (CH_2SO_2), and 22.5 ppm (CH_3). Found: C, 40.55; H, 5.54%. Calcd for $C_5H_8SO_3$: C, 40.52; H, 5.44%.

2,3-Dimethyl-1,3-butadiene δ-Sultone. In a similar manner, the reaction of 2,3-dimethyl-1,3-butadiene with the SO_3–DMF complex gave 3,4-dimethyl-3,6-dihydro-1,2-oxathiin 2,2-dioxide in an 18% yield; ^1H-NMR ($CDCl_3$): δ 4.70 (broad s, 2H, OCH_2), 3.55 (broad s, 2H, CH_2SO_2) and 1.77 ppm (two s, 6H, $2CH_3$): ^{13}C-NMR ($CDCl_3$): δ 122.8 and 119.6 (2>C=), 74.5 (CH_2O), 50.0 (CH_2SO_2), 19.1 and 13.8 ppm ($2CH_3$).

Dibromo δ-Sultone (4). A solution of 1.13 g (7.6 mmol) of **3** and 1.22 g (8.0 mmol) of bromine in chloroform (20 ml) was stirred at room temperature for 24 h. The reaction mixture was treated with $NaHSO_3$ aq to remove excess bromine. Extraction with chloroform and evaporation of the solvent followed by distillation gave 2.14 g (91%) of 4,5-dibromo-4-methyl-1,2-oxathiane 2,2-dioxide (**4**), bp 130 °C/5 mmHg, mp 99—100 °C; MS: *m/e* 227, 229 (M^+-Br, 40%); IR: 1170, 1360 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 5.1—4.4 (m, 3H, OCH_2-CHBr), 3.87 (s, 2H, CH_2SO_2) and 2.17 ppm (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$): δ 71.5 (OCH_2), 58.8 (CH_2SO_2), 57.6 ($-\overset{|}{\underset{|}{C}}-Br$), 52.8 (>CHBr), and 30.2 ppm (CH_3). Found: C, 19.41; H, 2.60%. Calcd for $C_5H_8Br_2SO_3$: C, 19.50; H, 2.62%,

Bromo δ-Sultone (5). A solution of 231 mg (0.75 mmol) of **4** and 1 ml of triethylamine in benzene (20 ml) was heated under reflux for 2 h. After filtration of triethylamine hydrobromide and evaporation of the solvent, distillation gave 163 mg (94.7%) of 5-bromo-4-methyl-5,6-dihydro-1,2-oxathiin 2,2-dioxide (**5**); bp 180 °C/16 mmHg, mp 129—130 °C, MS: *m/e* 226, 228 (M^+, 7%), 147 (M^+-Br, 100%); ^1H-NMR ($CDCl_3$): δ 6.10 (broad s, 1H, -CH=), 5.2—4.3 (m, 3H, OCH_2CHBr) and 2.15 ppm (d, 3H, CH_3); ^{13}C-NMR: δ 131.3 (>C=), 122.4 (-CH=), 73.9 (CH_2O), 41.7 (CHBr), and 21.6 ppm (CH_3). Found: C, 26.66; H, 3.08%. Calcd for $C_5H_7BrSO_3$: C, 26.45; H, 3.11%.

4-Methyl-5-methylene-1,2-oxathiole 2,2-Dioxide (6). To a solution of 680 mg (3 mmol) of **5** in *N,N*-dimethylformamide was added 127 mg (3 mmol) of lithium chloride and the reaction mixture was refluxed for 6 h. After the addition of water, the reaction mixture was extracted with benzene. The extract was washed with water to remove DMF and dried (Na_2SO_4). After removal of the solvent *in vacuo*, the residue crystallized. Recrystallization from ethanol gave 263 mg (60%) of **6**; mp 51—52 °C; MS: *m/e* 146 (M^+, 43%), 82 (M^+-SO_2, 14%); IR: 1650, 1600, 1440, 1330, 1180, 880, and 750 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 6.63 (broad s, 1H, -CH=), 4.87—5.22 (m, 2H, $=CH_2$) and 2.17 ppm (d, 3H, CH_3); ^{13}C-NMR: δ 152.2 and 142.7 (2 >C=), 121.1 (-CH=), 94.4 ($=CH_2$) and 12.2 ppm (CH_3); Found: C, 40.86; H, 4.36%. Calcd for $C_5H_6SO_3$: C, 41.15; H, 4.14%.

4-Methyl-1,2-oxathiin 2,2-Dioxide (1). To a solution of 1.05 g (4.6 mmol) of **5** and 1.3 ml of triethylamine in dichloromethane (20 ml) was added 0.90 g (4.6 mmol) of silver tetrafluoroborate. The reaction mixture was stirred for 48 h at room temperature. Removal of silver bromide by filtration and isolation by column chromatography on silica gel gave 125 mg (18.5%) of **1**; bp 120—125 °C/20 mmHg; MS: *m/e* 146 (M^+, 100%), 82 (M^+-SO_2, 20%); ^1H-NMR ($CDCl_3$): δ 6.96 (d, 1H, =CH-O), 6.38 (broad s, 1H, $=CH-SO_2$), 5.85 (d, 1H, -CH=), and 2.08 ppm (d, 3H, CH_3); ^{13}C-NMR: δ 145.8 (=CH-O), 145.6 (>C=), 116.4 ($=CHSO_2$), 109.3 (-CH=), and 21.6 ppm (CH_3). Found: C, 40.98; H, 4.28%. Calcd for $C_5H_6SO_3$: C, 41.15; H, 4.14%.

References

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