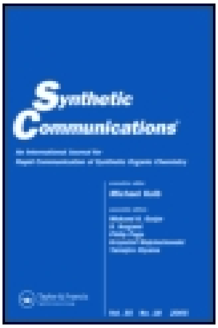

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Synthesis of vinyl Sulfones from 1,3-Dithiolane Tetraoxides

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SYNTHESIS OF VINYL SULFONES FROM 1,3-DITHIOLANE TETRAOXIDES

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Abstract: Vinyl sulfones are prepared in high yield by the treatment of 1,3-dithiolane tetraoxides with a catalytic amount of N,N-diisopropylethylamine in ethanol.

Vinyl sulfones are useful intermediates in organic synthesis,[1] and thus methods of preparing these compounds are of interest. In the course of a synthetic effort which involved the preparation of 1,3-dithiolane tetraoxides, we discovered a novel transformation that allows conversion of these compounds into vinyl sulfones in excellent yield. The 1,3-dithiolane tetraoxides (**3**) themselves are readily prepared

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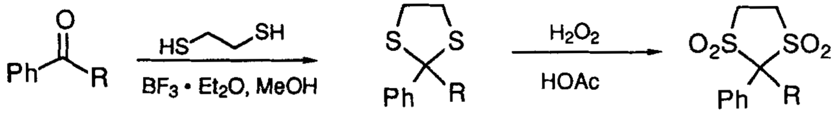
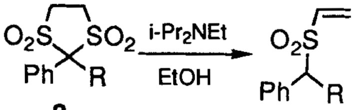


	R		Yield (%)		Yield (%)
1a	Me	**2a**	90	**3a**	75
b	Et	**b**	96	**b**	85
c	i-Pr	**c**	96	**c**	84
d	Ph	**d**	77	**d**	94

FIG. 1



3

(Crude yields all quantitative)

	Purity (%) (by NMR and GC)
5a	98
b	93
c	90
d	99

FIG. 2

in two steps via the dithioketalization/oxidation sequence shown in Figure 1 using known methodology.[2,3] As can be seen, yields are generally quite good.

The 1,3-dithiolane tetraoxides (**3**) can be converted in quantitative yield to vinyl sulfones (**5**) by treatment with a catalytic amount of N,N-diisopropylethylamine (Hünig's base) in ethanol (Figure 2). Other bases (EtONa, DABCO, t-BuOK, and NaH) also yielded the desired vinyl sulfones, though yields were highest using Hünig's base.

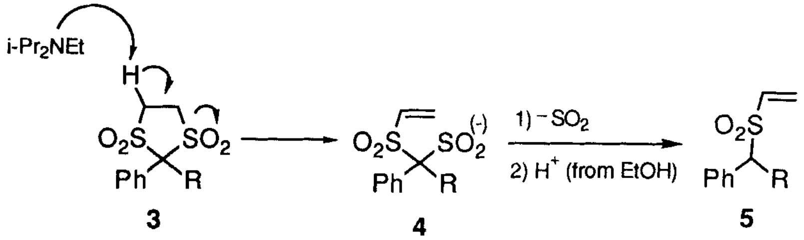


FIG. 3

A possible explanation of this transformation is shown in Figure 3. Deprotonation of (**3**) followed by ring opening would lead to sulfinate (**4**), while loss of SO_2 from (**4**) followed by protonation would produce vinyl sulfone (**5**).

Treatment of 1,3-dithiolane tetraoxides with alkoxides has previously been reported to yield β-alkoxysulfones,[4,5] presumably via Michael addition of the alkoxide to an intermediate vinyl sulfone. To the best of our knowledge, however, vinyl sulfones have not previously been isolated from the reaction of 1,3-dithiolane tetraoxides with base. The work described herein thus represents a novel approach to the preparation of these versatile compounds, which proceeds in just a few steps from readily available precursors.

Typical Preparation of Dithiolane Tetraoxides (**3**): To a solution of 1,3-dithiolane (**2**) (10 mmol in 5 mL HOAc) was added dropwise 4 to 5 equivalents of 30% H_2O_2. The resulting solution was stirred at 60-70 °C for 8 h, then diluted with water (5 mL). The precipitated product (**3**) was collected by filtration, washed with H_2O, and dried.

Typical Preparation of Vinyl Sulfones (**5**): To dithiolane tetraoxide (**3**) (1 mmol in 10 mL abs. EtOH) was added .05 eq. i-Pr_2NEt. The mixture was refluxed for the indicated time, then cooled to room temperature and diluted with 10 mL of saturated NH_4Cl solution. The mixture was extracted with $CHCl_3$ (3 x 20 mL), the combined organic extracts dried ($MgSO_4$), and solvent removed under reduced pressure.

Physical Data for Dithiolane Tetraoxides (3) and Vinyl Sulfones (5)

2-Methyl-2-phenyl-1,3-dithiolane-1,1,3,3-tetraoxide (**3a**) mp 133-5 °C (lit.[3] 133-4 °C).

2-Ethyl-2-phenyl-1,3-dithiolane-1,1,3,3-tetraoxide (**3b**) mp 136-8 °C; HRMS (CI, M + 1) calcd for $C_{11}H_{15}O_4S_2$ 275.0412, found 275.0419.

2-(1-Methylethyl)-2-phenyl-1,3-dithiolane-1,1,3,3-tetraoxide (**3c**) mp 160-2 °C (dec); HRMS (CI, M + 1) calcd for $C_{12}H_{17}O_4S_2$ 289.0568, found 289.0562.

2,2-Diphenyl-1,3-dithiolane-1,1,3,3-tetraoxide (**3d**)

mp 225-27 °C (dec); Anal. Calcd for: $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.38. Found: C, 55.77; H, 4.39.

1-Phenylethyl vinyl sulfone (**5a**)

Reaction time: 19 h; oil; HRMS (EI) calcd for $C_{10}H_{12}O_2S$ 196.0558, found 196.0560.

1-Phenylpropyl vinyl sulfone (**5b**)

Reaction time: 31 h; oil; HRMS (CI, M + 1) calcd for $C_{11}H_{15}O_2S$ 211.0793, found 211.0796.

2-Methyl-1-phenylpropyl vinyl sulfone (**5c**)

Reaction time: 41 h; oil; HRMS (CI, M + 1) calcd for $C_{12}H_{17}O_2S$ 225.0949, found 225.0951.

Diphenylmethyl vinyl sulfone (**5d**)

Reaction time: 21 h; mp 68-71 °C ;

Anal. Calcd for: $C_{15}H_{14}O_2S \cdot 1/2\ H_2O$: C, 67.39; H, 5.66. Found: C, 67.39; H, 5.51.

Spectral Data for Dithiolane Tetraoxides (3) and Vinyl Sulfones (5)

Cmpd	^1H NMR (250 MHz, $CDCl_3$)	^{13}C NMR (62.9 MHz, $CDCl_3$)
3 a	2.18 (s, 3H), 3.84 (s, 4H), 7.45-7.51 (m, 3H) 7.66-7.70 (m, 2H).	21.0, 49.0, 78.0, 126.3, 128.5, 130.11, 130.15.

3 b	1.06 (t, J = 7.3, 3H), 2.61 (q, J = 7.3, 2H), 3.72-3.84 (m, 4H), 7.44-7.52 (m, 3H), 7.62-7.66 (m, 2H).	9.1, 26.8, 49.5, 82.5, 127.5, 128.8, 129.3, 129.6.
3 c	1.21 (d, J = 6.9, 6H), 3.10 (sept, J = 6.9, 1H), 3.79(s, 4H), 7.43-7.46 (m, 3H), 7.82-7.86 (m, 2H).	19.0, 34.7, 50.9, 84.7, 128.3, 128.7, 129.3 (2 carbons).
3 d	3.94 (s, 4H), 7.37-7.48 (m, 6H), 7.56-7.64 (m, 4H).	49.8, 85.7, 128.7, 129.8, 130.4, 131.9.
5 a	1.70 (d, J = 7.2, 3H), 4.09 (q, J = 7.2, 1H), 6.06 (dd, J = 1.1, 8.6, 1H), 6.24-6.43 (m, 2H), 7.38 (s, 5H).	13.8, 64.2, 128.6, 128.8, 129.2, 131.2, 133.4, 134.1.
5 b	.88 (t, J = 7.4, 3H), 2.01-2.20 (m, 1H), 2.35-2.51 (m, 1H), 3.85 (dd, J = 3.9, 11.4, 1H), 6.01 (dd, J = 1.3, 8.4, 1H), 6.18-6.36 (m, 2H), 7.34 (s, 5H).	11.3, 20.9, 71.3, 128.7, 128.9, 129.7, 130.8, 131.9, 134.8.
5 c	.90 (d, J = 6.8, 3H), 1.28 (d, J = 6.6, 3H), 2.64-2.99(m, 1H), 3.76 (d, J = 8.1, 1H), 5.83 (dd, J = 1.0, 8.4, 1H) 6.06-6.34 (m, 2H).	20.6, 22.0, 28.7, 76.0, 128.3, 128.7, 129.2, 130.0, 132.8, 136.5
5 d	5.26 (s, 1H), 6.00 (d, J = 9.0, 1H), 6.30-6.51 (m, 2H), 7.32-7.43 (m, 6H), 7.60-7.64 (m, 4H).	74.7, 128.8, 128.9, 129.9, 130.9, 132.4, 135.8.

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