

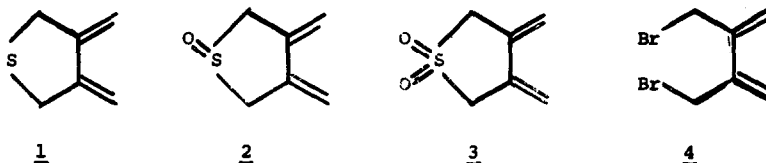
3,4-DIMETHYLENETHIOLAN, ITS 1-OXIDE AND 1,1-DIOXIDE

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Several attempts have been made in the past to prepare the 3,4-dimethylenethiolan 1<sup>1,2,3</sup> or, alternatively, its 1,1-dioxide, 3<sup>2</sup>. Some indirect evidence as to a low production of 1 was obtained only in one case<sup>3</sup>, but no pure adducts were described.



Thiolan 1, a dimethyl thiophene isomer, and its oxides are of potential interest in synthesis as 1,3-diene monomers or as starting materials in numerous addition reaction, including inter- or intramolecular cycloadditions. Another major interest of these compounds lies in the potential use of oxides 2 and 3 as precursors of the tetramethylenemethane biradical<sup>4</sup>, which might be formed from them by elimination of sulfur monoxide<sup>5</sup> or dioxide<sup>6</sup>, either thermally or photochemically.

We wish to report now a simple preparation of 1 and its oxidation to 2 and 3, as well as an alternative preparation of 3, and to describe a few of their addition products.

Reaction of dibromide 4<sup>7</sup> with sodium sulfide in ethanol gave 1 in 60% yield (estimated by UV). Thiolan 1 was obtained as an oil which polymerized rapidly in the free state. It could, however, be distilled in small batches and obtained pure for immediate

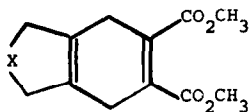
use (see Table for physical properties of compounds 1-3). Solutions of 1 were stable in diffuse daylight for at least one week and reactions in solution were carried out with very low extent of polymerization. Adducts of 1 were formed quite readily. Thus, with dimethyl acetylenedicarboxylate adduct 5a was obtained<sup>8</sup>, m.p. 136-137°,  $\delta$  (CDCl<sub>3</sub>), 3.08 s (6-membered ring protons), 3.73 s (5-membered ring protons) and 3.83 s (methyl ester).

Table. 3,4-Dimethylene thiolan and oxides

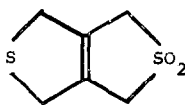
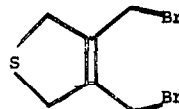
Comp.	M.p. °C	EtOH $\lambda_{\max}$ nm ( $\epsilon$ )	$\nu_{\max}$ cm <sup>-1</sup>	Proton chemical shifts <sup>a</sup>	
				Ring protons	Terminal methylene
<u>1</u>	B.p. 31 (1.5 mm)	240 (6000)	910 <sup>b</sup>	3.61	5.01, 5.45
<u>2</u>	67-68	244 (6150)	1020, 920, 900 <sup>c</sup>	3.70	5.29, 5.80
<u>3</u>	119 <sup>d</sup>	244 (6680)	1305, 1125, 1110, 925, 905, 880 <sup>c</sup>	3.93	5.23, 5.78

<sup>a</sup>At 60 MHz in CDCl<sub>3</sub>. All peaks were broadened singlets or finely split triplets, with splittings of 1.3-3.0 Hz due to allylic couplings. <sup>b</sup>In chloroform. <sup>c</sup>In KBr. <sup>d</sup>See text.

Addition of sulfur dioxide to 1 yielded sulfolene 6, m.p. 194° (sealed capillary), mass spectrum  $m/e$  176 (M<sup>+</sup>, base peak) and 112, 111 ( $\approx 100\%$ ), 97, 79, 77.  $\delta$  (CDCl<sub>3</sub>) 3.80 s (all protons),  $\delta$  (C<sub>5</sub>D<sub>5</sub>N) 3.67 s and 3.93 s (1:1).



5 a. X=S  
b. X=SO  
c. X=SO<sub>2</sub>

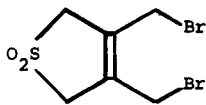
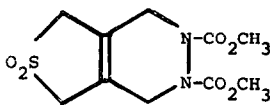
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Evidence for a 1,4 bromine addition to the diene system of 1 to give 7, was obtained when the reaction was carried out in the nmr tube: only two new singlets appeared at  $\delta$  3.93 and 4.06 along with the disappearance of the original peaks (compare to  $\delta$  4.02 and 4.07 for the corresponding sulfone 8<sup>9</sup>).

Oxidation of 1 to the sulfoxide 2 was carried out with sodium metaperiodate in acetonitrile<sup>10</sup> or better with *m*-chloroperbenzoic acid in chloroform at 0. The sulfoxide, obtained free of the sulfone, was purified by chromatography on silica gel (30% yield of isolated product) and recrystallization from hexane. Crystalline 2 polymerized overnight but its solutions were stable for several weeks. Mass spectrum (55°)  $m/e$  128 ( $M^+$ , base peak), 111, 85, 80, 79, 77. With dimethyl acetylenedicarboxylate adduct 5b was obtained, m.p. 145-146°,  $\delta$ (CDCl<sub>3</sub>) 3.20 s and 3.83 s (superimposed methyl and 5-membered ring protons; 2:5).

Sulfone 3 was obtained from 1 by oxidation with two moles of *m*-chloroperbenzoic acid in ether. It was purified by chromatography on silica gel (40% yield of isolated product) and recrystallization from pentane-ether. Mass spectrum (77°)  $m/e$  144 ( $M^+$ ), 80, 79 (base peak), 77. The solid sulfone was quite stable, being almost totally soluble after a few days at room temperature. Solutions of 3 were stable but traces of acid caused polymerization. Melting of the sulfone was observed only when a sample was introduced at the right temperature; by warming below the melting point insoluble, high melting transformation products were formed.

Adduct 5c of 3 with dimethyl acetylenedicarboxylate, m.p. 169-170°, was identical with the SO<sub>2</sub>-adduct of the corresponding diene, dimethyl 4,5-dimethylenecyclohexene-1,2-dicarboxylate<sup>7</sup>,  $\delta$ (CDCl<sub>3</sub>) 3.10 s and 3.63 s (superimposed methyl and five-membered ring protons; 2:5). With dimethyl azodicarboxylate, adduct 9 was obtained, m.p. 150-151°.

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An alternative preparation of sulfone 3 is the zinc-copper couple debromination of the dibromide 8, readily obtainable by bromination of 3,4-dimethylsulfone<sup>9</sup>. A low yield (~10%) of 3 was obtained when the reaction was carried out in ether-hexamethylphosphoramide or in dimethylformamide, but the optimum conditions for this reaction have perhaps not yet been found.

The chemical and thermal behaviour of compounds 1-3 are being further studied.

REFERENCES

1. C.S. Marvel and E.E. Ryder, *J.Amer.Chem.Soc.*, 77, 66 (1955).
2. C.S. Marvel, R.M. Nowak and J. Economy, *ibid.*, 78, 6171 (1956).
3. E.J. Fetter, *Dissertation Abstr.* 22, 2985 (1962).
4. J.J. Gajewski and C.N. Shih, *J.Amer.Chem.Soc.*, 94, 1675 (1972) and references therein.
5. For sulfur monoxide addition to dienes and the reverse dethionylation see P. Chao and D.L. Lemal, *J.Amer.Chem.Soc.*, 95, 920 (1973) and references therein.
6. For the use of the reversible cheletropic addition of SO<sub>2</sub> to dienes see H.W. Gschwend and H. Haider, *J.Org.Chem.*, 37, 59 (1972) and references therein.
7. Y. Gaoni, preceding communication.
8. Correct elemental analysis and other supporting data were obtained for all new isolated compounds (except 1).
9. G.B. Butler and R.M. Ottenbrite, *Tetrahedron Letters* 1967, 4873.
10. G.A. Russel and L.A. Ochrynowycz, *J.Org.Chem.*, 35, 2106 (1970).