

A NOVEL PREPARATION OF CYCLIC SULFITES THROUGH PHOTOSULFOXIDATION OF ALKENES

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Abstract—The cyclic sulfite, 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide, has been prepared by the photosulfoxidation of *trans*-2-pentene, and the quantum yield for the reaction has been determined. The proposed mechanism involves the reaction of a charge transfer complex formed between sulfur dioxide and the alkene, and is consistent with the participation of the triplet state of the former.

INTRODUCTION

The presence of 1,3,2-dioxathiolane 2-oxides (cyclic sulfites) in the photosulfoxidation products of alkenes was briefly reported in our recent preliminary communication¹; the photoreaction of *trans*-2-pentene with sulfur dioxide in the presence of oxygen has subsequently been studied in detail, and the photochemical preparation of the corresponding cyclic sulfite carried out. The formation of cyclic sulfites from reaction of thionyl chloride with the corresponding glycol is well documented;² the cyclic sulfites from 2,3-butanediol and 2,3-pentanediol were prepared in this manner to facilitate identification of the photoproduct.

EXPERIMENTAL

Photochemical preparation of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide from trans-2-pentene. *trans*-2-Pentene (99% Chem. Sample Co.), 10 g, was placed in a 50 ml Pyrex flask which was connected to an efficient spiral reflux condenser cooled to approximately -20° by $-PrOH$ circulated through a solid CO_2-PrOH bath. Two parallel tubes for the admission of O_2 and SO_2 entered through the neck of the flask, and dipped below the liquid surface. Illumination was provided by a water cooled 550 watt Hanovia medium pressure arc, situated directly below the flask. Radiation of wavelengths shorter than 290 nm was not transmitted by the flask wall. SO_2 (Matheson 99.9%) was further purified by bubbling through conc H_2SO_4 , and was admitted to the illuminated reaction flask at the same time as O_2 , both at approximately 10 ml min^{-1} over a period of 24 h. The product and excess alkene were dissolved in 1,4-dioxane and fractionated twice at reduced pressure. 9.4 g of alkene was recovered during the first fractionation, thus accounting for almost all of the starting material which was not converted to cyclic sulfite. 4-Ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide, 0.45 g, was collected at $80-82^{\circ}$ (12 mm). Gas chromatography combined with mass spectrometry showed that there were at least two isomeric products present which had identical mass spectra (chemical ionization with methane) (Fig 1). However, qualitative photosulfoxidation of *cis*-2-pentene followed by gas chromatographic analysis indicated that two further isomers of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide

were formed, which suggests that the alkyl group configuration of the alkene may be retained in the subsequently formed products.

The quantum yield for the formation of this cyclic sulfite was determined using apparatus similar to above, except the reaction flask was replaced by a 20 ml cylindrical 1 cm cell, and the gases were admitted through adjacent sintered discs situated below the light path. The cell was illuminated with a calibrated 75 watt P.E.K. high-pressure arc, equipped with Corning 7-54 and Pyrex glass filters; actinometry was accomplished by irradiating 1.5×10^{-2} moles liter⁻¹ solutions of potassium ferrioxalate in the reaction cell. The incident light intensity was 3.4×10^{-15} einsteins $cm^{-2} sec^{-1}$; under the conditions of the experiment, all of the incident light was absorbed by the saturated SO_2 in hydrocarbon soln. At the final product concentration (5×10^{-3} moles liter⁻¹) less than 0.1% of the incident light was absorbed by the product. After 10 h reaction, the excess alkene was distilled and the product made up to 10 ml in 1,4-dioxane; the yield of cyclic sulfite from two experiments was determined by gas chromatography and the quantum yield was calculated to be 0.04 ± 0.01 .

It was preliminarily demonstrated that photolysis of the $SO_2-trans$ -2-pentene charge transfer complex leads to the formation of the corresponding cyclic sulfite, by irradiation of this system using a Corning 0-52 filter which permits discrete excitation of the complex between 340 nm and 390 nm. However the absorbance of the complex at these wavelengths is insufficient to permit quantum yield determination. The product was identified as before by means of gas chromatography-chemical ionization mass spectroscopy.

Preparation of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide and 4,5-dimethyl-1,3,2-dioxathiolane 2-oxide from the corresponding diols. 2,3-Pentanediol (b.p. $185-8^{\circ}C/760$ mm) was prepared from the corresponding diketone by reduction with LAH³. The cyclic sulfites were separately prepared from 2,3-pentanediol and 2,3-butanediol by reaction with a 5% excess of $SOCl_2$. The products were fractionated at reduced pressure; 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide was collected at $82-85^{\circ}$ (12 mm) and 4,5-dimethyl-1,3,2-dioxathiolane 2-oxide at $74-76^{\circ}$ (12 mm). The respective boiling ranges at atmospheric pressure (760 mm) were $180-198^{\circ}$ and $175-188^{\circ}$, but the former sulfite very rapidly decomposed at this temp in contrast to the latter which appeared to be stable inde-

finitely. Preliminary gas chromatography (flame photometric detector) and GC-MS analysis [2.5 m × 1.5 mm, 1% OV-17 on Gas Chrom Q (Applied Science Labs)] showed that there are at least two geometric isomers of 4,5-dimethyl-1,3,2-dioxathiolane 2-oxide, and at least three geometric isomers of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxides (Figs 1 and 2). However, use of a

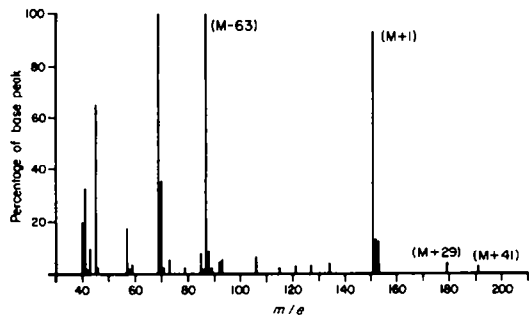


Fig 1. Mass spectrum (chemical ionization with methane) of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide

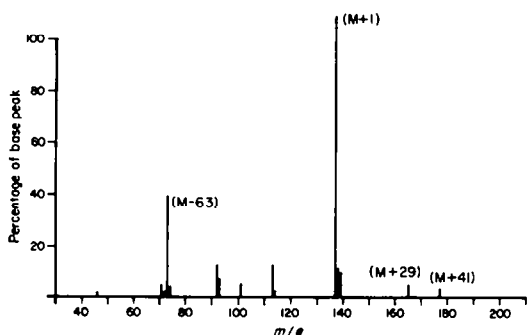


Fig 2. Mass spectrum (chemical ionization with methane) of 4,5-dimethyl-1,3,2-dioxathiolane 2-oxide

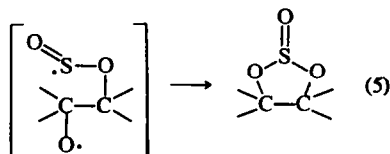
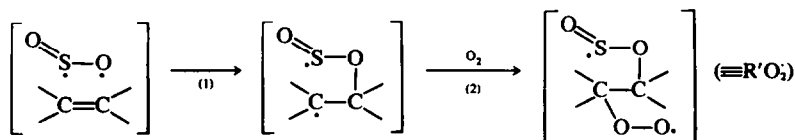
high polarity capillary column (12.5 m × 0.5 mm, Carbowax 20M/TPA (Perkin Elmer)) provided sufficient resolution for satisfactory separation of 3 and 4 isomers respectively. The 2 isomers of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide prepared photochemically from *trans*-2-pentene corresponded with the 2 isomers prepared

from the diol which had the longest retention time on the polar capillary column. The 2 isomers prepared from the diol with shortest retention time corresponded with the photochemical products from *cis*-2-pentene.

MECHANISM AND DISCUSSION

Charge transfer complexes between sulfur dioxide and hydrocarbons are well known^{4,9} and the equilibrium constant for the formation of the *trans*-2-pentene complex is approximately 0.2 mole⁻¹ litres.^{4,9} Under the prevailing reaction conditions, about half of the sulfur dioxide is expected to be complexed with alkene. The absorption spectrum of sulfur dioxide in cyclohexane solution shows a maximum at 290 nm. However, in the presence of an alkene the absorption broadens and extends to longer wavelengths because of absorption by the resulting charge-transfer complex; such sulfur dioxide-alkene complexes exhibit an absorption maximum at 315 nm and extend to approximately 390 nm.⁹

We propose that the initial reactions in the formation of cyclic sulfites by alkene photosulfoxidation include singlet excitation of sulfur dioxide, followed by intermolecular or intramolecular conversion to the triplet state;¹⁰ there is considerable evidence that the predominantly reactive state of sulfur dioxide is the triplet.¹¹⁻¹⁴ The participation of triplet in preference to singlet sulfur dioxide in alkene photosulfoxidation is also preferred on the grounds that it may reasonably give rise to C-O bond formation (see later also), whereas the singlet may lead to C-S bonding through insertion into the π bond of the alkene. However, in order to mechanistically explain the formation of cyclic sulfites, we suggest that a complex incorporating triplet sulfur dioxide is the important first step towards product formation. Since both the sulfur dioxide and the complex absorb light, triplet sulfur dioxide can result from direct excitation of sulfur dioxide or from excitation of the complex. Following the attack of the triplet on the π bond of the alkene, oxidation at the carbon radical would be expected to lead to the cyclic sulfite by the following sequence of reactions:



Reaction (2) would be expected to be the fastest step in the reaction scheme, because of its very low activation energy.¹⁵ However, reactions (1) and (2) may in fact occur as a single step; an electrophilic attack on the complex by molecular oxygen would be expected to take place at the carbon atom adjacent to sulfur, in view of the electronegativity difference between the sulfur and oxygen of the sulfur dioxide molecule. It appears that the cyclic sulfites retain the alkyl group configuration which was originally present in the parent alkene, which suggests that reactions (1) and (2) may indeed occur in a time short compared with bond rotational times, in order that free rotation at the site of the π bond may be sterically hindered.

Reaction (4) would be expected to have a relatively high activation energy,¹⁶ although the unpaired electron on sulfur may induce homolytic fission of the peroxide bond and result in an increased rate of cyclization. The formation of the intermediate in reaction (1), as opposed to the alternative carbon-sulfur bonded intermediate, is favored on the grounds of relative bond energies, overall entropy change, and the enhanced radical stabilization by sulfur.¹

When considering the magnitude of the quantum yield for the formation of 4-ethyl-5-methyl-1,3,2-dioxathiolane 2-oxide, the quantum yield for the conversion of singlet to triplet sulfur dioxide must be taken into account since the overall quantum yield cannot exceed the triplet yield if the cyclic sulfite is formed by the proposed mechanism; this latter quantum yield is 0.09 ± 0.06 .¹⁰ The large error limits do not permit detailed comments, but our experimental value of 0.04 ± 0.01 for cyclic sulfite formation is consistent with the role of triplet sulfur dioxide in the proposed mechanism.

Quantum yield considerations also serve to eliminate the photo-oxidation of sulfur dioxide to sulfur trioxide as a precursor of the sulfite. The maximum quantum yield for sulfur dioxide photo-oxidation is 5×10^{-3} ,¹⁷ a value too low to be consistent with our observed quantum yield for cyclic sulfite formation. Furthermore, the reaction of ethylene tetrafluoride with sulfur trioxide has been shown to produce 3,3,4,4-tetrafluoro-1,2-oxathietane 2,3-dioxide, and only when sulfur dioxide was likely to be present were traces of 4,4,5,5-tetrafluoro-1,3,2-dioxathiolane 2-oxide (a cyclic sulfite) additionally formed.¹⁸ Thus, the data presently available are consistent with the proposed

mechanism for cyclic sulfite formation through triplet sulfur dioxide.

We have previously pointed out that cyclic sulfites may be important constituents of photochemical smog, since their formation may be possible in an atmospheric aerosol.¹ Cyclic sulfites are structurally similar to several potent carcinogens (sultones, lactones and epoxides), and they may be equally efficient as alkylating agents. We hope to investigate the chemistry of cyclic sulfites in a future study, and in particular to examine their alkylating reactions in an attempt to determine the likelihood of their being carcinogenic.

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