active homogenate from the whole coral. Approximately 200 mg of wet algae cells in 12 ml of a pH 8.0 buffer (0.05 M tris and 1 M NaCl) was passed twice through a French press at 12,000 psi. Two milliliters of this homogenate was used for the incubation. After 40 min at 28°, none of the 20 μg of the tritiated eicosatrienoic acid had been converted to PGA$_1$. These are the standard conditions for conversion of eicosatrienoic acid to PGA$_1$ by homogenates of *Plexaura homomalla*.[3] It was also found that no appreciable amounts of A prostaglandins could be detected in the whole algal cells by extraction with ether–ethyl acetate and the analysis of the concentrated extracts. It is quite clear from these results that the prostaglandin synthetase is contained in the coral cells, not in the algae.

Although the results of the above investigation are disappointing from the viewpoint of possible large scale *in vitro* biosynthesis of prostaglandins, they raise several interesting points for further research, especially in the completely undeveloped area of the biochemistry of symbiotic relationships between coral and their algal guests. Also still to be determined are the factors which govern the rates of arachidonic acid synthesis, transport from algae to coral, and conversion to prostaglandins.[9]

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Decomposition of 3,6-Dihydro-1,2-oxathiin 2-Oxides to Sulfur Dioxide and 1,3-Dienes. A $_\pi4_s + _\pi2_s$ Cycloreversion

Sir:

The concerted addition of sulfur dioxide to 1,3-dienes to give 2,5-dihydrothiophene 1,1-dioxide is well known.[1] The reverse of this reaction has also been studied in detail[2] and has been classified as one of a family of symmetry allowed cheletropic reactions.[3] The stereospecific elimination of SO$_2$ from episulfones[4] and 2,7-dihydrothiepin 1,1-dioxides[5] is an additional example of this type of fragmentation reaction.

We would like to report that 3,6-dihydro-1,2-oxathiin 2-oxides fragment into SO$_2$ and 1,3-dienes. This transformation is stereospecific and is apparently the first example of the formation of SO$_2$ and 1,3-dienes *via* a $_\pi4_s + _\pi2_s$ cycloreversion (retro-Diels–Alder). It occurs with remarkable ease, at least 150–200° below that of the cheletropic reaction producing the same products (eq 1). The $_\pi4_s + _\pi2_s$ cycloaddition of SO$_2$ to 1,3-dienes is apparently not observable because of the presence of the more favorable process leading to 2,5-

(1) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 2.

(2) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 152–163.

(4) For a review see N. H. Fischer, *Synthesis*, 393 (1970).

(5) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967); (b) *ibid.*, **91**, 5682 (1969); (c) *ibid.*, **92**, 3807 (1970).

dihydrothiophene 1,1-dioxides. N-Sulfenylamines (RN=S=O)[6] and sulfines (R$_2$=C=S=O)[7] which have considerable structural analogy to SO$_2$ readily take part in $_\pi4_s + _\pi2_s$ cycloadditions.

$$(1)$$
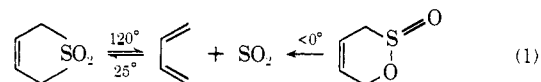
The ease of the above $_\pi4_s + _\pi2_s$ cycloreversion is illustrated by the following observations. Reaction of the cis hydroxy sulfoxide 2[8,9] with N-chlorosuccinimide in CH$_2$Cl$_2$ at 0°[10] led to immediate SO$_2$ evolution and formation of 1,3-butadiene (>90% vpc). 3,6-Dihydro-1,2-oxathiin 2-oxide (3), the expected product of the reaction of 2 with NCS,[10] is therefore unstable and decomposes rapidly to SO$_2$ and 1,3-butadiene even at 0°. In contrast, the rapid formation of these two products from the isomeric 2,5-dihydrothiophene 1,1-dioxide requires temperatures above 120°.[1]

The stereospecific nature of the 3,6-dihydro-1,2-oxathiin 2-oxide decomposition was shown by the conversion of the cis hydroxy sulfoxide 4, prepared as shown in Scheme I, to isomerically pure *trans*-1-phenyl-1,3-buta-

Scheme I
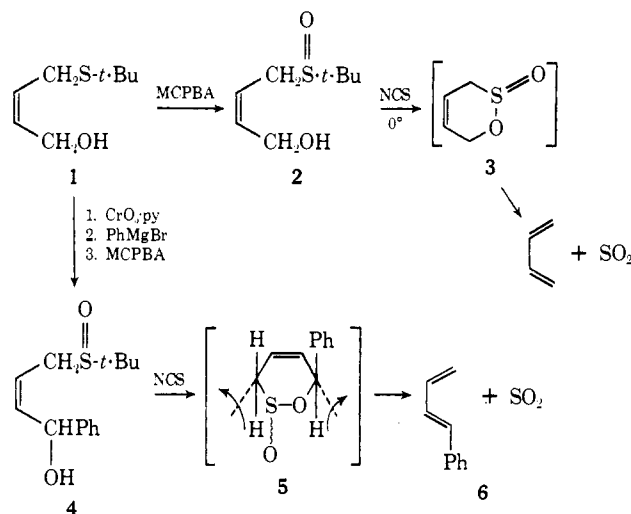
diene (6).[11] In the fragmentation of the intermediate 5 to diene and SO$_2$ a steric effect superimposed on the disrotatory motion at C$_3$ and C$_6$ would account for the formation of only 6.[12] The formation of isomerically pure 6 from 5, which was undoubtedly a mixture of diastereomers,[13] indicates that the sulfur–oxygen stereochemistry may be of negligible importance in determin-

(6) G. Kresze, ref 1, Chapter 13.

(7) B. Zwanenberg, L. Thijs, J. B. Broens, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **91**, 443 (1972).

(8) All new numbered compounds gave correct analyses.

(9) Prepared from cis-2-butene-1,4-diol *via* the monotetrahydropyranyl ether, mesylation thereof, followed by reaction with *tert*-butyl mercaptide, deprotection and oxidation.

(10) N. K. Sharma, F. Jung, and T. Durst, *Tetrahedron Lett.*, 2863 (1973); F. Jung, N. K. Sharma, and T. Durst, *J. Amer. Chem. Soc.*, **95**, 3420 (1973).

(11) Vpc analysis of the product and comparison with a mixture containing both the cis and trans isomer (O. Grummitt and F. J. Christoph, *J. Amer. Chem. Soc.*, **73**, 3479 (1951)) indicated that 6 was >99.5% isomerically pure.

(12) A similar argument can be used to explain the formation of pure *trans*-1,3-pentadiene in the decomposition of 2-methyl-2,5-dihydrothiophene 1,1-dioxide.

(13) Cyclization of a diastereomeric mixture of 7b and of one isomer of 7b gave the same diastereomeric mixture of oxathiin 2-oxide (8b). This shows that the cyclization is not stereospecific and that, in general, a diastereomeric mixture can be expected.

ing the direction of rotation of the substituents at C_2 and C_6 during the cycloreversion.

In order to prepare a stable 3,6-dihydro-1,2-oxathiin 2-oxide, we turned our attention to the benz-fused compounds **8**. The required hydroxy sulfoxides, **7**, were readily prepared from phthalide as shown in Scheme II.

Scheme II
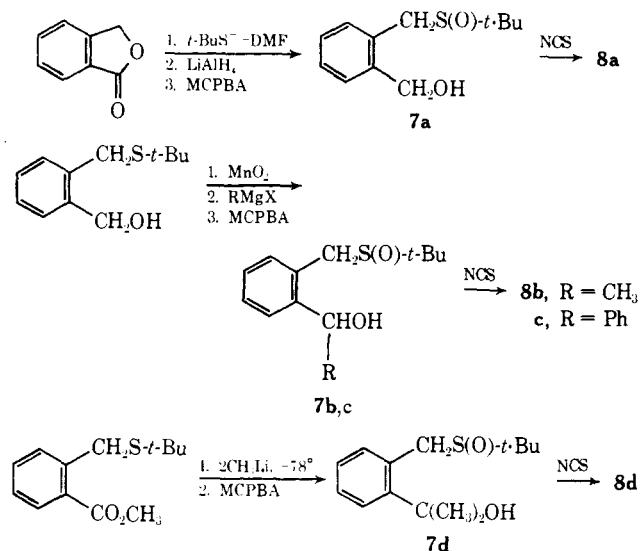
Reaction of **7a–d** with NCS gave **8a–d** in 75–95 % yield. When the parent compound **8a**[14] was heated in refluxing benzene it cleanly isomerized to 1,3-dihydrobenzo[c]-thiophene 2,2-dioxide (**10a**)[15] ($t_{1/2}$ = 6 hr). That this isomerization represented a cycloreversion to o-quino-dimethane (**9a**) and SO_2 followed by a typical SO_2 + 1,3-diene cycloaddition[16] was shown by carrying out the thermolysis in the presence of a very reactive dienophile such as maleic anhydride. Under these conditions the tetrahydronaphthalene derivative, **11**,[17] was obtained in over 95 % yield. The sulfinate esters **8** have thus considerable potential as precursors for the generation of variously substituted o-quinodimethanes under very mild conditions.[18] In contrast to the above, the generation of o-quinodimethane from the sulfone **10a** requires heating in refluxing diethylphthalate (300°) for approximately 1 hr.[16] These results again illustrate the ease with which SO_2 is lost in a retro-Diels–Alder reaction from 3,6-dihydro-1,2-oxathiin 2-oxides compared to the cheletropic extrusion from the isomeric 2,5-dihydrothiophene 1,1-dioxide.

The designation of the SO_2 extrusion from **3, 5,** and **8** as a $_\pi 4_s$ + $_\pi 2_s$ cycloreversion implies concertedness and stereospecificity for these reactions. The results obtained with **5** indicate, but do not conclusively prove, these properties.[19] The variations in the relative rates

(14) Colorless oil; nmr CH_2 α to S at δ 3.51 and 4.37 (J = 15 Hz), CH_2 α to O at δ 4.91 and 5.27 (J = 14 Hz); ir 1105 cm⁻¹ (S=O).

(15) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959).

(16) See F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962); and F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.*, **80**, 6149 (1958) for an example of the addition of SO_2 to a substituted o-quinodimethane.

(17) R. D. Haworth and F. H. Slinger, *J. Chem. Soc.*, 1321 (1940).

(18) A number of groups have recently utilized the electrocyclic ring opening of benzocyclobutenes as a route to o-quinodimethanes. These reactions are reported to occur at temperatures ranging from 110 to 200°: B. J. Arnold and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, **30**, 1074 (1972); W. Oppolzer, *J. Amer. Chem. Soc.*, **93**, 3833 (1971).

(19) It would have been preferable to have substituents of known stereochemistry at both C_3 and C_6 in the oxathiin. We have not been able to prepare such a system up to this point.
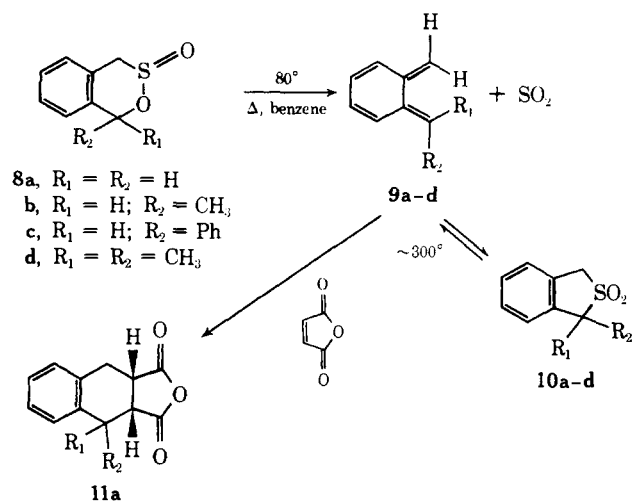
of rearrangement of the oxathiins **8** to the sulfones **10** (**8a**:**8b**:**8c**:**8d** = 1.0:1.9:200:0.023) and the insensitivity of the rates to solvent change (**8a**; benzene vs. CH_3CN = 1.0:1.3) are not in agreement with a dipolar or diradical intermediate resulting from initial C–O bond cleavage. They are more reasonable on the basis of a concerted loss of SO_2 from **8** → **9**, followed by rapid reaction of **9** + SO_2 → **10**. The oxathiine **8b** and **8c** would be expected to react faster than the parent compound because of the stabilization by the substituent of the intermediates **9b** and especially **9c**; **8d** should be strongly retarded because of an adverse steric effect which prevents **9d** from becoming planar.[20,21]

(20) Similar effects have been observed in the ring opening of cis- and trans-1,2-diphenylbenzocyclobutene to the expected o-quinodimethanes: R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Weisdorf, and M. Finke, *ibid.*, 3009 (1965).

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Duality of Mechanism in the Electrophilic Bromination of Aromatic Compounds[1,2]

Sir:

In an aromatic substitution reaction, a bond is formed and a bond is broken. If the substitution reagent furnishes no electrons to the new bond, the substitution is termed "electrophilic."

Conceptually, the timing of bond making and bond breaking for straightforward substitution at a single site may conform to one of three patterns: (1) the new bond from aromatic carbon to electrophile may form first, after which the old bond to the electrofugic substituent ruptures; (2) formation of the new bond may be concerted with rupture of the old bond; or (3) the old bond may break first, after which the new bond forms.

The first pattern is familiar in the many aromatic electrophilic substitutions which proceed via σ-complex intermediates; the electron pair needed to form

(1) Based on the Ph.D. Thesis of M. H. Mach, University of California, Santa Cruz, 1973.

(2) Research supported in part by the National Science Foundation.