group at position 4 clearly had the composition -CHD-CHD_2.[2] A reversal of this substitution pattern would have given an ethyl group with the composition -CDH-CDH_2. The observed composition after isotope reversal, however, was $CD_{\sim 1.4}H_{\sim 0.6}$–$CD_{\sim 2.4}H_{\sim 0.6}$. Further, it was clear that this substitution pattern was not due to the presence of only two chemical species (*e.g.*, -CD_2CD_3 and -CDH-CDH_2), since the shape of the resonances under deuterium decoupling suggested that the predominant hydrogen species was -CHD-CHD_2 that was mixed with several other hydrogen species. One explanation for these nmr observations would be that the enzymes responsible for the transformation of the propionic acid side chain at position 6 into ring V may operate on the side chains, at positions 4 and 7 (and 2) in the deuterio organisms, but not in the protio organisms, to give an acrylic acid type side chain at some stage in the biosynthesis.

The 1 and 5 methyl resonances from the D_2O–succinate-h_4 derived methyl bacteriopheophorbide showed a reversal of the isotope substitution pattern observed for the isotope mirror organisms within experimental error, whereas the 3 and 8′ resonances did not. The number of protons at the 3 and 8′ positions showed an increase over the expected isotope mirror composition. The 3 and 8′ positions must have undergone less exchange in the D_2O medium than in H_2O. The 3 and 8′ areas relative to the 1 and 5 resonances in the pheophorbide derived from the D_2O–succinate-h_4 grown bacteria were virtually the same. This suggests that, in the organisms grown on D_2O and succinate-h_4, the chemical history of the four ring-methyl groups could have been very similar. In the isotope reverse of this experiment, however, there were substantial differences either in the chemical modifications of the methyl groups or in the exchange reactions with the medium.

The methyl ester function at position 11 for the D_2O–succinate-h_4 derived organisms showed a substitution pattern suggesting the synthesis of this group from succinate followed identical courses in the two different growth media.

We believe that the experiments described here illustrate a procedure that may be widely applicable to the study of chemical reactions in living organisms.

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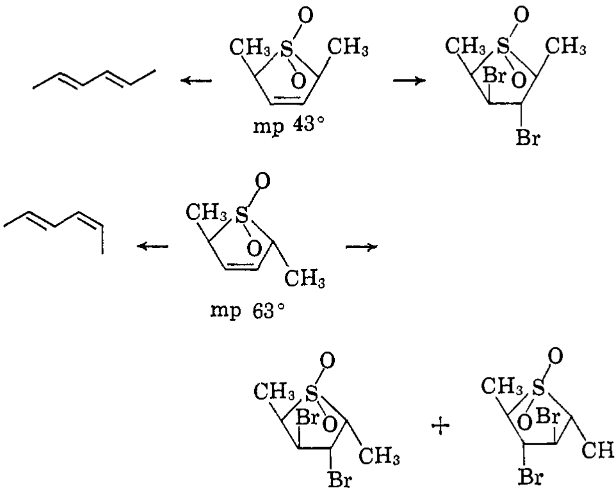
The Stereoelectronic Course of the Diene–Sulfur Dioxide Reaction

Sir:

We wish to report that the 1,4 addition of sulfur dioxide to conjugated acyclic dienes is a concerted *cis* addition or in the recently introduced terminology[1] is a disrotatory process.[2] This conclusion follows from a study of the retroreaction involving the isomers of 2,4-hexadiene.

The known isomer of 2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide, mp 43° (*Anal.* Found: C, 49.12; H, 6.80), was prepared according to Backer[3] and crystallized from pentane. Chromatography of the mother liquor on alumina (hexane–benzene eluent) provided a second isomer, mp 63–63.5° (*Anal.* Found: C, 49.89; H, 6.67). Upon vapor phase pyrolysis at 200° and 1 mm of argon pressure in a rapid flow system with subsequent trapping and analysis by vapor phase chromatography[4] these substances gave *trans,trans*- and *trans,cis*-2,4-hexadiene, respectively, with greater than 99.9% stereospecificity.



Configurational assignments for the isomeric 2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxides are based on the nmr spectra of their corresponding dibromides. The nmr spectrum of the dibromide, mp 123–124° (*Anal.* Found: C, 23.57, H, 3.45), of the isomer affording *trans,trans*-2,4-hexadiene shows nonequivalent methyl groups (τ 8.47 and 8.51, doublets, $J = 6.9$ and 7.2 cps in $CDCl_3$) and therefore has methyl groups *cis* to one another, assuming *trans* addition of bromine to the double bond.[5] The other isomer afforded two dibromides in unequal amount, each possessing equivalent methyl groups as shown by nmr (τ 8.47 and 8.49, doublets, both $J = 6.7$ cps). Hence this isomer has methyl groups *trans* to one another. The more abundant dibromide, mp 88–88.5° (*Anal.* Found: C, 23.97; H, 3.25), was isolated by fractional crystallization from hexane.

The importance of steric factors in this decomposition is revealed by the facts that the *cis*-dimethyldihydrothiophene dioxide gives only *trans,trans*-2,4-hexadiene and no *cis,cis*-2,4-hexadiene[6] and that the decomposition temperature of the *trans*-dimethyldihydrothiophene dioxide is 50° higher in the neat liquid than that of the *cis* isomer (150 *vs.* 100°, vigorous gas evolution). This latter observation cannot be ascribed to destabilization of the *cis* isomer relative to the *trans* isomer due to steric repulsion by the methyl groups since at equilibrium this species predominates. Equilibration was achieved from either isomer in 3–4 days

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[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[2] The decomposition in cases involving cyclic dienes is necessarily disrotatory: W. L. Bailey and E. W. Cummings, *ibid.*, **76**, 1936, 1940 (1954).

[3] H. J. Backer, J. Strating, and C. M. H. Kool, *Rec. Trav. Chim.*, **58**, 778 (1939).

[4] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

[5] This conclusion was confirmed by the formation of an osmium tetroxide–pyridine adduct of the olefin in which the methyl groups are equivalent in the nmr spectrum.

[6] Only *trans*-piperyline is obtained from 2-methyl-2,5-dihydrothiophene 1,1-dioxide: D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

at 100° in liquid sulfur dioxide; $K_{cis/trans} = 1.5$, determined by nmr spectroscopy.[7]

These results demonstrate the following points. (1) The dissociation of these adducts is a concerted process (or nearly so). The alternative would be a two-step mechanism involving dipolar[8] or diradical intermediates. That such intermediates would not result in the observed stereospecificity has been demonstrated.[4] (2) This 1,4 elimination is *cis* or disrotatory. This direction is that predicted by the principles presented by Woodward and Hoffmann[1] (assuming an elementary molecular orbital description of sulfur dioxide[9]).

We note, however, that for this particular ring system electronic factors may not be expected to be dominant. We envisage as the vibrational deformation leading to the transition state folding of the five-membered ring with the departing SO_2 fragment out of the plane of the four ring carbon atoms.[10] This model is in accord with the steric factors previously mentioned. Any conrotatory process would require relatively greater C–S bond rupture before appreciable overlap is developed within the incipient conjugated system. It is difficult to assess how the difference in activation energy between the processes thus represented compares with that expected from symmetry considerations alone. Since decomposition of thiirane 1,1-dioxide is also a stereospecific *cis* elimination[7] and is therefore presumably concerted, the role of stereoelectronic factors in electrocyclic transformations involving sulfur dioxide cannot yet be conclusively adjudged.

(7) This isomer distribution is perhaps another manifestation of the factors which preferentially yield *cis*-substituted olefins from α-chlorosulfones and base: N. P. Neurieter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1210 (1963).

(8) O. Crummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950).

(9) W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950).

(10) A geometrically similar transition state has been postulated in the decomposition of 1-pyrazolines: R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965).

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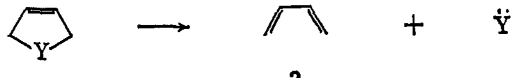
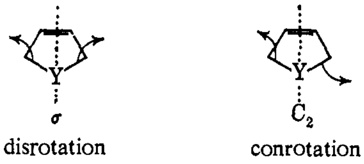
Fragmentations. The Thermal 5 → 4 + 1 Reaction[1]

Sir:

Although there exist many examples of thermal five-membered ring fragmentations of the type **1** → **2** where Y = >C=O, >N⁺=N⁻, and $>SO_2$,[3] the question of ring-opening stereochemistry has been answered only in part. If concerted, decomposition must occur in either of two modes: disrotatory or conrotatory,[2] illustrated below. All three systems are predicted on the basis of orbital symmetry arguments to fragment thermally *via* the former pathway.[2c] This has been verified for the diazene.[4] Rigid model compounds have afforded evidence that 3-cyclopentenones and 3-sulfolenes *can* fragment with disrotation,[5] but clear-cut stereochemical experiments on unconstrained ketones and sulfones have not been reported. We now wish (1) to describe such experiments in the sulfolene series, and (2) to consider the behavior of **1** (Y = >NNO), for which only the conrotatory mode is symmetry allowed.[2c]



1 **2**



trans,trans-2,4-Hexadiene was allowed to react at room temperature with excess sulfur dioxide in the presence of pyrogallol to give a single sulfolene (**3**), 70% after sublimation, mp 44–44.2° after recrystallization of the sublimate from carbon tetrachloride (lit.[6] mp 43–43.5°). The much slower addition of sulfur dioxide to *cis,trans*-2,4-hexadiene required elevated temperatures, and isomerization occurred. After 12 hr at 96° **3** and an isomeric 3-sulfolene (**4**, isolated by fractional crystallization from carbon tetrachloride, mp 64.8–65.2°)[7,8] were obtained in roughly equal amounts.

Pyrolyses of **3** and **4** were carried out most conveniently in the injection chamber of a vapor chromatograph fitted with a Ucon Polar on Chromosorb W (HMDS-treated) column operated at 35°. At normal flow rates and an injector temperature of 155°, **3** was completely cleaved while **4** was left unscathed; this contrast in lability made separation of **4** from mixtures of the isomers extremely easy. For complete destruction of **4** it was necessary to raise the injector temperature to about 245°. In addition to sulfur dioxide, the only pyrolysis product of sulfolene **3** detectable by vapor chromatography was *trans,trans*-2,4-hexadiene, and **4** gave only the *cis,trans* diene. Intercontamination to the extent of 1% would have been observed in these experiments. Thus fragmentation and, by the principle of microscopic reversibility, formation of these sulfolenes as well are cleanly stereospecific processes.

cis-2,5-Dimethyltetrahydrothiophene, prepared from *meso*-2,5-dibromohexane and purified *via* its mercuric chloride complex, was oxidized with peracetic acid to the sulfone.[9] This sulfolane was identical with the product from hydrogenating **3** and easily distinguishable from the hydrogenation product of **4**. Hence **3**

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(1) The nomenclature is based on Huisgen's classification of cycloaddition reactions (R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., London, 1964, p 739). In terms of the number of electrons primarily involved, these fragmentations would be designated "6 → 4 + 2."[2b]

(2) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (c) Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8S; private communication.

(3) See, for example: (for ketones) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); (for diazenes) W. Baker, J. F. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961); L. A. Carpino, *J. Am. Chem. Soc.*, **84**, 2196 (1962); ref 4; (for sulfones) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950); W. L. Bailey and E. W. Cummings, *ibid.*, **76**, 1936, 1940 (1954); M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959); M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

(4) D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

(5) Baldwin has concluded from a kinetic study that thermal decarbonylation of cyclopentadienone dimer is concerted. The process is necessarily disrotatory, then, because of the geometrical requirements of the fused ring system (J. E. Baldwin, private communication). The facility with which Diels–Alder adducts of thiophene dioxide with itself and other dienophiles lose sulfur dioxide suggests that their decomposition is also concerted, and thus disrotatory (Bailey and Cummings, ref 3).

(6) H. J. Backer, J. Strating, and C. M. H. Kool, *Rec. Trav. Chim.*, **58**, 778 (1939).

(7) All new compounds prepared in this study gave correct elemental analyses.

(8) Their nmr spectra established that both sulfolenes were Δ^3 isomers.

(9) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).