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THERMALLY AND PHOTOCHEMICALLY INDUCED ELIMINATION OF SULFUR OXIDES FROM 2,5-DIHYDROTHIOPHENE-S-OXIDES AND S-DIOXIDES

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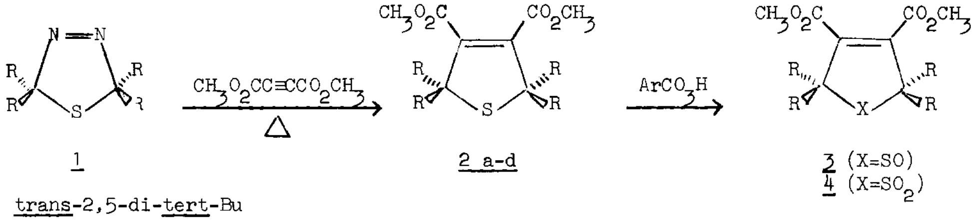
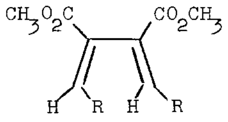
We observe that the 2,5-dihydrothiophene derivatives 3 and 4 lose the respective sulfur oxides on either photochemical or thermal activation. The organic products are the dienes 5-8, the stereochemistry of which affords insight into the mechanism of fragmentation.

The synthesis of starting materials was carried out as shown in eq 1.[1] Stereochemical assignments for 3 and 4, obtained by oxidation of 2 with the requisite amount of meta-chloroperbenzoic acid ($ArCO_3H$), were made following previously developed arguments.[1,2]

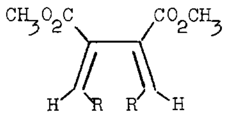


a) trans-2,5-di-tert-Bu
b) trans-2,5-dimethyl
c) cis-2,5-dimethyl
d) 2,2,5,5-tetramethyl

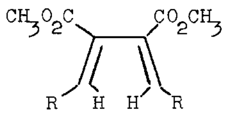
(1)



5a-c



6a-c



7a-c

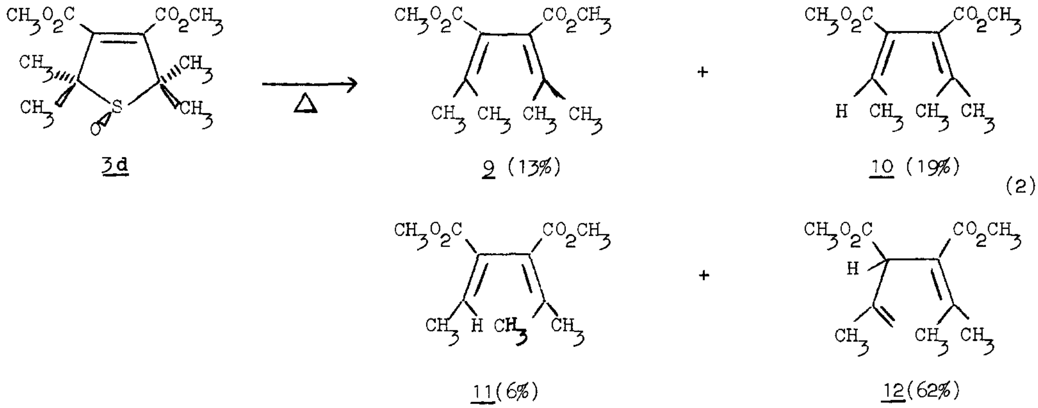
Irradiation of 3,4a-c in D_3COD (Philips SP-500 lamp, room temp) or pyrolysis (210-350°) gave 5-7a-c, for which stereochemical assignments have been made previously.[1,3] Yields were >80% in preparative thermolyses and quantitative in analytical runs; photochemical reactions were quantitative as determined by nmr. Pertinent stereochemical data are given in Table I.

Table I

	Products					
Compound	Δ^a 5	$h\nu^{b,c}$	Δ^a 6	$h\nu^{b,c}$	Δ^a 7	$h\nu^{b,c}$
3a	75%	57%	12%	25%	13%	18%
4a	99	72	1	10	1	18
3b	95	79	2.5	21	2.5	0
4b	100	58	0	29	0	13
3c	10	37	6	52	84	11
4c	0	36	0	64	100	0

a) Analytical data using glass-lined injector port of glpc; product ratios are not measurably temperature dependent.
b) Nmr analyses used as 3,4 are thermally unstable; product ratios are constant in range of 10 - 40% conversion.
c) Starting materials were not detectably isomerized during reaction.

Thermolysis of 3d, however, provided anomalous results. Although sulfone 4d afforded exclusively 9 on photolysis or thermolysis and 3d gave also 9 on photolysis, the thermal reaction of 3d yielded the product mixture shown in eq 2. Separation was accomplished by preparative glpc; 10 - 12 were characterized fully by ir, nmr, and mass spectral analyses (including europium shift reagent experiments with 12).



3d

9 (13%)

10 (19%)

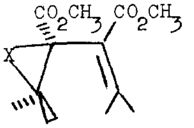
(2)

11(6%)

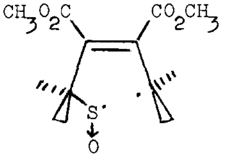
12(62%)

Loss of sulfur dioxide from 4a-d is entirely anticipated and when thermally induced, conforms both to the rigid steric constraints attending a concerted elimination as well as to orbital symmetry demands.[5] Inspection of Table I reveals that such is also the case with 4a-c, in which the diene component participates exclusively suprafacially.

At least as a first approximation, photochemical excitation should lead to reversed (antarafacial) stereochemical features.[5] Despite obvious steric constrictions, analogs of 4a-c, lacking substitutions in the 3,4-positions, show a tendency to behave in this manner.[6] With 4a-c such is clearly not the case; on this basis one could argue perhaps that sulfur dioxide does not depart in a concerted process from these compounds but rather that a stepwise mechanism obtains. We note that the fragmentation stereochemistry resembles markedly that involved in photochemically induced loss of sulfur from 2,5-dihydrothiophenes 2; these reactions involve ring contraction to vinyl episulfides (13,X=S), which subsequently lose sulfur stereospecifically.[3] Unfortunately, all our attempts to observe (probably very unstable) episulfone intermediates (13,X=SO_2) have thus far failed.



13(X=S,SO,SO_2)



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Similar arguments apply for the photochemical reactions of 3a-c. Again the isomer distribution, which resembles that from 4a-c, is not readily brought into agreement with any reasonable application of simple orbital symmetry conservation arguments. The intervention of thus far unisolated vinyl episulfoxide intermediates (13,X=SO) is a reasonable possibility.

Contrary to recently published results,[7] thermally induced elimination of sulfur monoxide from 3a-c is reasonably stereoselective and proceeds also in high yield. Lemal and Chao observed that the addition of sulfur monoxide to simple dienes proceeded with good stereoselectivity,[8] but that this stereoselectivity was lost in the retroreaction. However, the less than 100% stereoselectivity (as seen with 4a-c) provides at least circumstantial evidence for the transitory existence of a biradical 14˙. The deviate behavior of 3d, in which, among other things, overall loss of the elements of sulfine occurs, likely is the result of intramolecular trapping of 14•, followed by a complex reaction sequence.

We suggest that a significant orbital symmetry induced barrier denies a concerted route to the sulfoxide pyrolyses(despite similar bond energies for the C-S bonds in allylic sulfoxides and sulfones).[9] This point becomes particularly explicit in reasoning developed by Pearson.[10] For concerted elimination of sulfur monoxide from 2,5-dihydrothiophene-S-oxides with disrotatory participation of the diene component, the breaking bonds have A' and A" symmetry *(in C_s point group), the π orbital has A' symmetry, and in product butadiene the filled MO's are* A' and A" but the antibonding MO of sulfur monoxide to be filled has A" symmetry.[11] Hence the reaction coordinate cannot be totally symmetric and the reaction is orbital symmetry forbidden.[10] In elimination of sulfur dioxide this problem is avoided for the MO to be filled has the correct A' symmetry.

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4. See for example: (a) W.L. Mock, *ibid*., **88**, 2857 (1966); (b) S.D. McGregor and D.M. Lemal, *ibid*., **88**, 2858 (1968); (c) also W.L. Mock, *ibid*., **91**, 5682 (1969).
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